รายงานวิจัยฉบับสมบูรณ์

โครงการ ผลของตะกั่วส่วนเกินที่มีต่อสมบัติของเซรามิกเลดแบเรียมเซอร์โคเนต

โดย

ผู้ช่วยศาสตราจารย์ ดร. ธีระชัย บงการณ์
มหาวิทยาลัยนเรศวร

มิถุนายน 2551

รหัสสัญญา MRG4980163

รายงานวิจัยฉบับสมบูรณ์

โครงการ ผลของตะกั่วส่วนเกินที่มีต่อสมบัติของเซรามิกเลดแบเรียมเซอร์โคเนต

ผู้ช่วยศาสตราจารย์ ดร. ธีระชัย บงการณ์

มหาวิทยาลัยนเรศวร

สนับสนุนโดยสำนักงานคณะกรรมการการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกว.ไม่จำเป็นต้องเห็นด้วยเสมอไป)

กิตติกรรมประกาศ

งานวิจัยนี้สำเร็จได้ด้วยดีเนื่องจากการสนับสนุนทุนวิจัยจาก สำนักงานกองทุนสนับสนุนการวิจัย (สกว.) และ สำนักงานคณะกรรมการอุดมศึกษา (สกอ.) ขอขอบคุณ คณะวิทยาศาสตร์ มหาวิทยาลัยนเรศวรที่อำนวยความสะดวกในการใช้เครื่องมือ สถานที่ ขอขอบคุณ ห้องปฏิบัติการอิเล็กโทรเซรามิก คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่ ที่สนับสนุนเครื่องมือวิเคราะห์ รวมไปถึงการช่วยเหลือที่ดีจากผู้ร่วมวิจัย ผู้วิจัยขอขอบคุณ รองศาสตราจารย์ ดร. กอบวุฒิ รุจิจนากุล ที่รับเป็นที่ปรึกษา และ ให้คำปรึกษาที่ดีตลอดมา ขอบคุณผู้ร่วมวิจัย ผู้ช่วยศาสตราจารย์ ดร.อรวรรณ ฤทธิเดช ดร. นราธิป วิทยากร และนักศึกษาทุกคนที่ช่วยกันทำงานอย่างเข้มแข็ง สุดท้าย ขอขอบคุณ บิดา มารดาที่เป็นกำลังใจ และ ให้การสนับสนุนด้วยดีตลอดมา

ผู้ช่วยศาสตราจารย์ ดร.ธีระชัย บงการณ์
หัวหน้าโครงการ

เอกสารแนบหมายเลข 2

บทคัดย่อ

---

1. รหัสโครงการ: MRG4980163

2. ชื่อโครงการ ผลของตะกั่วส่วนเกินที่มีต่อสมบัติของเซรามิกเลดแบเรียมเซอร์โคเนต

3. ชื่อหัวหน้าโครงการ

ผู้ช่วยศาสตราจารย์ ดร. ธีระชัย บงการณ์

ภาควิชา ฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยนเรศวร

ถนนพิษณุโลก-นครสวรรค์ อ.เมือง จ.พิษณุโลก 65000

E-mail Address: researchcmu@yahoo.com, theerachaib@nu.ac.th

4. ระยะเวลาดำเนินงาน 2 ปี (1 มิถุนายน 2549 ถึง 30 มิถุนายน 2551)

บทคัดย่อ

เตรียมเซรามิกเลดแบเรียมเซอร์โคเนต ($(Pb_{1-x}Ba_x)ZrO_3$, $0.025 \leq x \geq 0.100$) ด้วยวิธีปฏิกิริยาสถานะของแข็ง เติมตะกั่วส่วนเกินปริมาณร้อยละ 1, 3, 5 และ 10 โดยน้ำหนัก ลงในสารตั้งต้นก่อนการเผาแคลไซน์เพื่อชดเชยตะกั่วที่ระเหยไประหว่างการขบวนการเผา เผาแคลไซน์ที่อุณหภูมิ 1000 องศาเซลเซียส เป็นเวลา 1 ชั่วโมง และเผาซินเตอร์ที่อุณหภูมิ 1300 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง วิเคราะห์โครงสร้างเฟสโดยเครื่องเลี้ยวเบนรังสีเอกซ์ (XRD) พบเฟสแปลกปลอมของตะกั่วออกไซด์ในผงผลึกที่มีการเติมตะกั่วส่วนเกินปริมาณร้อยละ 3-10 โดยน้ำหนัก ในขณะที่พบเฟสบริสุทธิ์ของโครงสร้างเพอร์รอฟสไกต์ในทุกตัวอย่างของเซรามิก ค่าคงที่ไดอิเล็กทริกและความหนาแน่นมีค่าสูงสุดเมื่อเติมตะกั่วส่วนเกินปริมาณร้อยละ 1 โดยน้ำหนัก ศึกษาการเปลี่ยนแปลงเฟสโดยใช้เครื่อง differential scanning calorimeter (DSC) พบว่าการเปลี่ยนแปลงเฟสจากเฟร์โรอิเล็กทริก (FE) ไปเป็นเฟร์โรอิเล็กทริก (AFE) ของเซรามิกเลดแบเรียมเซอร์โคเนต ขณะที่ทำให้เย็นตัวลงขึ้นอยู่กับปริมาณของตะกั่วส่วนเกินที่เติมเข้าไปในสารตั้งต้น ในองค์ประกอบที่ x= 0.075 และ 0.100 ไม่พบการเปลี่ยนแปลงเฟสของ FE⟶AFE เมื่อไม่เติมตะกั่วส่วนเกิน แต่จะพบการเปลี่ยนแปลงเฟสของ FE⟶AFE เมื่อเติมตะกั่วส่วนเกินปริมาณร้อยละ 5-10 โดยน้ำหนัก ในองค์ประกอบที่ x= 0.025 และ 0.050 เกิดการเปลี่ยนแปลงเฟสของ FE⟶AFE แม้ไม่เติมตะกั่วส่วนเกิน แต่อุณหภูมิในการเปลี่ยนแปลงเฟสจะเพิ่มขึ้นประมาณ 30-40 องศาเซลเซียส เมื่อเติมตะกั่วส่วนเกินมากกว่าร้อยละ 1 หรือ 3 โดยน้ำหนัก ตามลำดับ ปริมาณของตะกั่วส่วนเกินมีผลต่อการเปลี่ยนแปลงเฟสของ FE⟶AFE โดยมีปริมาณเพิ่มขึ้นเมื่อองค์ประกอบ x เพิ่มขึ้น

คำหลัก: เลดแบเรียมเซอร์โคเนต, ตะกั่วส่วนเกิน, แอนติเฟร์โรอิเล็กทริก, สมบัติไดอิเล็กทริก, การเปลี่ยนเฟส

เอกสารแนบหมายเลข 2

Abstract

Project Code: MRG4980163

Project Title: Effect of Excess PbO on The Properties of Lead Barium Zirconate Ceramics

Investigator: Assistant Professor Dr. Theerachai Bongkarn

E-mail Address: researchcmu@yahoo.com, theerachaib@nu.ac.th

Project Period: 2 years (1 June 2006 ถึง 30 June 2008)

Polycrystalline samples of $(Pb_{1-x}Ba_x)ZrO_3$, $0.025 \leq x \geq 0.100$ were prepared by a mixed oxide, solid-state reaction method. Excess PbO (1, 3, 5 and 10 wt%) was introduced prior to powder calcination to compensate for any PbO that may have been lost from the samples due to volatilsation during heat treatments. The samples were kept at the calcinations temperature 1000° C for 1 h and at the sintering temperature 1300° C for 3 h. The phase structure was analyzed by XRD. For calcined powders,The small amount of PbO was present in the 3-10 wt% excess PbO samples. On the other hand, pure perovskite $(Pb_{1-x}Ba_x)ZrO_3$ phase was observed in all of the ceramic samples. The density of the ceramics decreases with increasing amount of Ba^{2+}, whilst the average grain size is in the range 0.6 – 1.6 μm. Dielectric constant-temperature plots showed a maximum peak for the 1 wt% sample which was also the densest sample. Phase transitions were also investigated using differential scanning calorimeter (DSC). The temperature and existence of ferroelectric (FE) to antiferroelectric (AFE) cooling phase transitions in $(Pb_{1-x}Ba_x)ZrO_3$ ceramics, were shown to depend on the level of excess PbO in the starting powders. Without excess PbO, no FE⟶AFE cooling transition is observed in ε_r-T or DSC plots for x = 0.075 or 0.100 compositions, but additions of 5-10 wt% PbO generate the transition. For x = 0.025 and 0.050, the FE⟶AFE transitions occur without excess PbO but $T_{FE\text{-}AFE}$ are raised by ~30-40 °C on adding ≥1 wt% or ≥3 wt% PbO respectively. The amount of extra PbO required to affect the FE-AFE transition increases with increasing Ba^{2+} substitution.

Key words: lead barium zirconate, excess PbO, antiferroelectric, dielectric properties, phase transition

1. Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

ผลงานตีพิมพ์ในวารสารวิชาการระดับนานาชาติจำนวนทั้งสิ้น 10 เรื่อง

1. ***T. Bongkarn*** and G. Rujijanagul, “Effect of Excess PbO on Microstructure and Mechanical Properties of $(Pb_{0.975}Ba_{0.025})ZrO_3$ ceramics” Current Applied Physics, 6(2006)319-322.**(impact factor 1.117)**
2. G. Rujijanagul, A. Rittidech and ***T. Bongkarn***, “Phase Formation, Piezoelectric and Mechanical Properties of $(Pb_{1-x}Ba_x)ZrO_3$ Ceramics” Materials Science and Engineering A-Structural, 438-440(2006)360-363. **(impact factor 1.490)**
3. A. Rittidech, L. Portia and ***T. Bongkarn***, “The relationship between microstructure and mechanical properties of Al_2O_3-MgO ceramics” Materials Science and Engineering A-Structural, 438-440(2006)395-398. **(impact factor 1.490)**
4. Naratip Vittayakorn, ***Theerachai Bongkarn*** and Gobwute Rujijanagul, “Phase transion, dielectric and piezoelectric properties of perovskite $(Pb_{1-x}Ba_x)ZrO_3$ ceramics ” Physica B: Condensed Matter, 387(2007)415-420. **(impact factor 0.872)**
5. G. Rujijanagul and ***T. Bongkarn***, “Phase transition and linear thermal expansion of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics” Phase Transitions, 80(2007)209-215. **(impact factor 0.830)**
6. Naratip Vittayakorn and ***Theerachai Bongkarn*** “Influence of strontium doping on the ferroelectrics and piezoelectric properties of lead zinc niobate-lead zirconate titanate ceramics” Ferroelectrics, 358:1(2007)54-59. **(impact factor 0.459)**

7. ***Theerachai Bongkarn*** and Gobwute Rujijanagul, “Effect of excess lead oxide on phase transition and physical properties of perovskite lead barium zirconate ceramics” Ferroelectrics, 358:1(2007)67-73. **(impact factor 0.459)**
8. Gobwute Rujijanagul, Naratip Vittayakorn and ***Theerachai Bongkarn***, “Effect of barium substitution on phase transition of lead barium zirconate ceramics prepared by solid state reaction method” Ferroelectrics, 355:1(2007)84-89. **(impact factor 0.459)**
9. A. Rittdech, L. Chaisangka, R. Tipakorntitikul and ***T. Bongkarn***, “Investigation of phase formation of (1-*x*)PMN-*x*PT in morphotropic phase boundary” Ferroelectrics, 355:1(2007)77-83. **(impact factor 0.459)**
10. ***T. Bongkarn***, G. Rujijanagul and S.J. Milne, “Antiferroelectric phase transitions in $Pb_{1-x}Ba_xZrO_3$ Ceramics: Effect of PbO Content” Applied Physics Letters, 92(2008)092905-1-3. **(impact factor 3.979)**

2. การนำผลงานวิจัยไปใช้ประโยชน์

- **เชิงพาณิชย์**
  โครงการวิจัยนี้ได้สร้างองค์ความรู้ใหม่เกี่ยวกับปริมาณของตะกั่วส่วนเกินที่เหมาะสมในการเตรียมรวมทั้งผลของปริมาณตะกั่วส่วนเกินที่มีต่อสมบัติต่างๆของเซรามิกPBZ ซึ่งสามารถนำไปประยุกต์ใช้ในเชิงพาณิชย์ และเป็นองค์ความรู้พื้นฐานของอุตสาหกรรมได้เป็นอย่างดี
- **เชิงนโยบาย**
  ผลงานที่ได้จากโครงการวิจัยนี้ได้ ใช้เป็นตัวกำหนดทิศทางงานวิจัยที่จะทำต่อยอดในอนาคต และใช้เป็นส่วนช่วยในการกำหนดหัวข้อวิจัยในมุมมองอื่นๆสำหรับนักศึกษา และผู้ร่วมวิจัยในสาขาอื่นๆ ซึ่งเป็นประโยชน์ในการเชื่อมโยงองค์ความรู้ให้เกิดหลากหลายมากขึ้น
- **เชิงสาธารณะ**
  โครงการวิจัยนี้ได้เกิดเครือข่ายงานวิจัยกับหลากหลายภาคส่วนด้วยกันทั้งในองค์กรภายในมหาวิทยาลัยและองค์กรนอกมหาวิทยาลัย เช่น รองศาสตราจารย์ ดร. กอบวุฒิ รุจิจนากุล

จากห้องปฏิบัติการอิเล็กโทรเซรามิก จาก ภาควิชาฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่ ความร่วมมือกับ ผู้ช่วยศาสตราจารย์ ดร. อรวรรณ ฤทธิเดช จาก ภาควิชาฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยมหาสารคาม ดร.นราธิป วิทยากร จาก ภาควิชาเคมี คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง ผู้วิจัยได้มีโครงการความร่วมมือกับนักวิจัยต่างประเทศหลายท่าน อาทิเช่น Prof. Dr. Steven J. Milne จาก Institute for Materials Research, University of Leeds ประเทศอังกฤษ Prof. Dr. Tadashi Takenaka จาก Department of Electrical Engineering, Tokyo University of Science ประเทศญี่ปุ่น และ Prof. Dr. David P. Cann จาก ห้องปฏิบัติการอิเล็กโทรเซรามิก มหาวิทยาลัยโอเรกอน ประเทศสหรัฐอเมริกา

- **เชิงวิชาการ**

  ผลงานวิจัยที่เกิดขึ้นบางส่วนนำไปประยุกต์ใช้สอนในกระบวนวิชาเซรามิกไฟฟ้า ในระดับบัณฑิตศึกษา นอกจากนั้นประสบการณ์ที่ได้จากงานวิจัยยังสามารถนำไปประยุกต์ อบรมเจ้าหน้าที่และ ผู้ช่วยวิจัยให้มีทักษะและความชำนาญมากยิ่งขึ้น ก่อให้เกิดองค์ความรู้ในองค์กร ผลงานวิจัยส่วนใหญ่สามารถตีพิมพ์ในวารสารระดับนานาชาติ รวมไปถึงการเสนอผลงานวิจัยในงานประชุมวิชาการที่เกี่ยวข้องทั้งในระดับชาติและนานาชาติ อีกทั้งยังเกิดนักวิจัยรุ่นใหม่ขึ้น

3. อื่น ๆ (เช่น ผลงานตีพิมพ์ในวารสารวิชาการในประเทศ การเสนอผลงานในที่ประชุมวิชาการ หนังสือ การจดสิทธิบัตร)

ผลงานตีพิมพ์ในวารสารระดับชาติจำนวนทั้งสิ้น 12 เรื่อง

1. ***T. Bongkarn***, C. Puchmark, N. Vittayakorn and G. Rujijanagul “TG, DTA, XRD and SEM Studies of $(Pb_{0.90}Ba_{0.10})ZrO_3$ Ceramics” Journal of Microscopy Society of Thailand, 20(1) (2006)120-121.
2. C. Puchmark, ***T. Bongkarn***, N. Vittayakorn and G. Rujijanagul “Effect of Heating Rate and Dwell Time on the Grains Size of Lead Zirconate Titanate” Journal of Microscopy Society of Thailand, 20(1) (2006)118-119.
3. Naratip Vittayakorn, Chompoonuch. Puchmark and ***Theerachai Bongkarn***, “Phase and Morphology Investigateion of Perovskite $(Pb_{1-x}Ba_x)ZrO_3$ Ceramics” Journal of Microscopy Society of Thailand, 20(1) (2006)87-88.

4. Naratip Vittayakorn, Chompoonuch. Puchmark and ***Theerachai Bongkarn***, “Phase and Morphology Investigateion of PZT-based Powders Prepared by Columbite-(Wolframite) Precursor” Journal of Microscopy Society of Thailand, 20(1) (2006)85-86.
5. Naratip Vittayakorn and ***Theerachai Bongkarn***, “Preparation of Zirconium Titanate ($ZrTiO_4$) Powders via Mixed Oxide Synthesis Route” Journal of Microscopy Society of Thailand, 20(1) (2006)83-84.
6. Naratip Vittayakorn and ***Theerachai Bongkarn***, “Phase formation and crystal structure of 0.9PZT-0.1PZN powders prepared by columbite” NU Science Journal, 2(2)(2006)157-164.
7. Naratip Vittayakorn and ***Theerachai Bongkarn***, “Phase and morphology evolution of zirconium titanate powders” NU Science Journal, 3(1)(2006)21-28.
8. Naratip Vittayakorn and ***Theerachai Bongkarn***, “Phase formation, permittivity and piezoelectric properties of perovskite $(Pb_{1-x}Ba_x)ZrO_3$ ceramics” KMITL Science Journal, 6 (2006) 590-598.
9. ***Theerachai Bongkarn*** and Naratip Vittayakorn “Effect of excess PbO on phase formation, microstructure and dielectric properties of $(Pb_{0.975}Ba_{0.025})ZrO_3$ ceramics” NU Science Journal, 3(2)(2007)111-117.
10. ***Theerachai Bongkarn*** and Perapong Panya, “Effect of calcination temperatures on crystal structure and morphology of $(Pb_{0.90}Ba_{0.10})TiO_3$ powders” NU Science Journal, 4(1)(2007)67-76.

11. ***Theerachai Bongkarn***, Nalinee Phungjit and Naratip Vittayakorn, “Effect of calcination temperatures on microstructure and phase formation of crystal structure and morphology of $Ba(Zr_{0.3}Ti_{0.7})O_3$” NU Science Journal, 4(S1)(2007)13-21.
12. ***Theerachai Bongkarn*** and Saichol Sukkhon, “Effect of ZrO_2 doping on crystal structure and microstructure of lead titanate ceramics” NU Science Journal, 4(2)(2008) 195-203.

การนำเสนอผลงานวิจัยในงานประชุมวิชาการทั้งสิ้น 34 เรื่อง

1. ***T. Bongkarn***, C. Puchmark, N. Vittayakorn and G. Rujijanagul “TG, DTA, XRD and SEM Studies of $(Pb_{0.90}Ba_{0.10})ZrO_3$ Ceramics” The 23rd Annual Conference of The Microscopy Society of Thailand, Bangkok, Thailand (2006).
2. C. Puchmark, ***T. Bongkarn***, N. Vittayakorn and G. Rujijanagul “Effect of Heating Rate and Dwell Time on the Grains Size of Lead Zirconate Titanate” The 23rd Annual Conference of The Microscopy Society of Thailand, Bangkok, Thailand (2006).
3. Naratip Vittayakorn, Chompoonuch. Puchmark and ***Theerachai Bongkarn***, “Phase and Morphology Investigateion of Perovskite $(Pb_{1-x}Ba_x)ZrO_3$ Ceramics” The 23rd Annual Conference of The Microscopy Society of Thailand, Bangkok, Thailand (2006).
4. Naratip Vittayakorn, Chompoonuch. Puchmark and ***Theerachai Bongkarn***, “Phase and Morphology Investigateion of PZT-based Powders Prepared by Columbite-(Wolframite) Precursor” The 23rd Annual Conference of The Microscopy Society of Thailand, Bangkok, Thailand (2006).

5. Naratip Vittayakorn and ***Theerachai Bongkarn***, “Preparation of Zirconium Titanate ($ZrTiO_4$) Powders via Mixed Oxide Synthesis Route” The 23rd Annual Conference of the Microscopy Society of Thailand, Bangkok, Thailand (2006).
6. Naratip Vittayakorn and ***Theerachai Bongkarn***, “Phase transion, dielectric and piezoelectric properties of perovskite $(Pb_{1-x}Ba_x)ZrO_3$ ceramics” KMITL International Conference on Science and Applied Science 2006, Bangkok, Thailand (2006).
7. Naratip Vittayakorn, ***Theerachai Bongkarn*** and Gobwute Rujijanagul “Synthesis and Electrical Properties of Bismuth Doped Barium Titanate Ceramics” 2006 International Conference on Micro/Nano Fabrication Technologies (ICM/NFT’06), Bangkok, Thailand (2006).
8. G. Rujijanagul and ***T. Bongkarn***, “Phase transition and linear thermal expansion of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics” Asia-Pacific Conference of Transducers and Micro-Nano Technology 2006 (APCOT2006), Singapore (2006).
9. ***Theerachai Bongkarn*** and Gobwute Rujijanagul, “Effect of excess lead oxide on phase transition and physical properties of perovskite lead barium zirconate ceramics” The 5th Asian Meeting on Ferroelectrics (AMF-5), Noda, Japan (2006).
10. Gobwute Rujijanagul, Naratip Vittayakorn and ***Theerachai Bongkarn***, “Effect of barium substitution on phase transition of lead barium zirconate ceramics prepared by solid state reaction method” The 5th Asian Meeting on Ferroelectrics (AMF-5), Noda, Japan (2006).
11. Naratip Vittayakorn, ***Theerachai Bongkarn*** and Gobwute Rujijanagul, “Influence of strontium doping on the ferroelectrics and piezoelectric properties of lead zinc

niobate-lead zirconate titanate ceramics" The 5th Asian Meeting on Ferroelectrics (AMF-5), Noda, Japan (2006).

12. A. Rittdech, L. Chaisangka and ***T. Bongkarn***, "Investigation of phase formation of (1-*x*)PMN-*x*PT in morphotropic phase boundary" The 5th Asian Meeting on Ferroelectrics (AMF-5), Noda, Japan (2006).
13. Nalinee Phungjitt, Naratip Vittayakorn and ***Theerachai Bongkarn*** "Effect of calcination temperature on microstructure and phase formation of $Ba(Zr_xTi_{1-x})O_3$ powders" Asian Symposium on Materials and Processing 2006 (ASMP 2006), Bangkok, Thailand (2006).
14. Perapong Panya, and ***Theerachai Bongkarn*** "Effect of calcination temperature on phase formation and morphology of lead barium titanate powders" Asian Symposium on Materials and Processing 2006 (ASMP 2006), Bangkok, Thailand (2006).
15. Perapong Panya, and ***Theerachai Bongkarn*** "Microstructure and Structural Phase of Perovskite $(Pb_{0.975}Ba_{0.025})TiO_3$ Powders" The 5th Asian Meeting on Electroceramics (AMEC-5), Bangkok, Thailand (2006).
16. ***Theerachai Bongkarn*** and Gobwute Rujijanagul "Properties of $(Pb_{0.90}Ba_{0.10})ZrO_3$ Ceramics with Deficient and Excess PbO" The 5th Asian Meeting on Electroceramics (AMEC-5), Bangkok, Thailand (2006).
17. ***T. Bongkarn***, N. Phungjitt, N. Vittayakorn "Preparation and characterization of $Ba(Ti_{0.8}Zr_{0.2})O_3$ powders via solid state reaction method" International Conference on Engineering, Applied Sciences, and Technology (ICEAST 2007), Bangkok, Thailand (2007).

18. ***T. Bongkarn***, P. Panya, N. Vittayakorn “Preparation and characterization of lead barium titanate powders via high temperature solid state reaction” International Conference on Engineering, Applied Sciences, and Technology (ICEAST 2007), Bangkok, Thailand (2007).
19. ***T. Bongkarn***, T. Patanin, P. Panya and A. Thongtha “Phase Formation and Microstructure of Barium Modified Lead Titanate Powders” The 25th Annual Conference of the Electron Microscopy Society of Thailand (MST25), Phitsanulok, THAILAND (2008).
20. ***T. Bongkarn***, P. Sittikethron and W. Tangkawsakul “Effect of Excess PbO on Crystal Structure and Microstructure of Lead Titanate Powders” The 25th Annual Conference of the Electron Microscopy Society of Thailand (MST25), Phitsanulok, THAILAND (2008).
21. ***T. Bongkarn***, S. Chootin, S. Sukkho and P. Sittikethron “Effect of Sintering Heating Rate on Phase Formation and Microstructure of Lead Titanate Ceramics” The 25th Annual Conference of the Electron Microscopy Society of Thailand (MST25), Phitsanulok, THAILAND (2008).
22. ***T. Bongkarn***, N. Phungjitt and N. Vittayakorn “Phase Formation and Microstructure of $Ba(Zr_{0.20}Ti_{0.80})O_3$ Ceramics Prepared via Solid State Reaction Method” The 25th Annual Conference of the Electron Microscopy Society of Thailand (MST25), Phitsanulok, THAILAND (2008).
23. ***T. Bongkarn***, S. Chootin, R. Sumang and J. Wattanawikkam “Effect of Excess PbO on Phase Formation and Microstructure of $(Pb_{0.925}Ba_{0.075})TiO_3$ Powders” The 25th

Annual Conference of the Electron Microscopy Society of Thailand (MST25), Phitsanulok, THAILAND (2008).

24. ***T. Bongkarn*** and C. Thiangchit "Phase Formation and Microstructure of PBZT Powders Prepared via Mixed Oxide Method" Smart/Intelligent Materials and Nano Technology 2008 (SmartMat-08), Chiang Mai, THAILAND (2008).

25. P. Sittiketkron, S. Sukkho and ***T. Bongkarn*** "Effect of ZrO_2 Doping on Crystal Structure, Microstructure and Phase Transition of Lead Titanate Ceramics" Smart/Intelligent Materials and Nano Technology 2008 (SmartMat-08), Chiang Mai, THAILAND (2008).

26. ***T. Bongkarn***, N. Phungjitt, N. Vittayakorn and A. Thongtha "Effect of Calcination Temperatures on Microstructure and Phase Formation of $Ba(Zr_{0.25}Ti_{0.75})O_3$ Powders" Smart/Intelligent Materials and Nano Technology 2008 (SmartMat-08), Chiang Mai, THAILAND (2008).

27. A. Thongtha, K. Angsukased and ***T. Bongkarn*** "Effects of Calcination Temperatures on Phase and Morphology Evolution of $(Ba_{0.25}Sr_{0.75})$ $(Zr_{0.75}Ti_{0.25})O_3$ Powders Synthesized via Solid-State Reaction and Combustion Technique" Smart/Intelligent Materials and Nano Technology 2008 (SmartMat-08), Chiang Mai, THAILAND (2008).

28. ***T. Bongkarn*** and P. Panya "Fabrication of Lead Barium Titanate Ceramics via Conventional Solid-State Mixed Oxide Technique" Smart/Intelligent Materials and Nano Technology 2008 (SmartMat-08), Chiang Mai, THAILAND (2008).

29. C. Wattanawikkam and ***T. Bongkarn*** “Fabrication of Barium Stannate Tatanate Ceramics via Combustion Technique” Smart/Intelligent Materials and Nano Technology 2008 (SmartMat-08), Chiang Mai, THAILAND (2008).

30. W. Tangkawsakul, P. Sittiketkron and ***T. Bongkarn*** “Effect of Excess PbO on Crystal Structure, Microstructure and Phase Transition of Lead Titanate Ceramics” Smart/Intelligent Materials and Nano Technology 2008 (SmartMat-08), Chiang Mai, THAILAND (2008).

31. W. Tangkawsakul, P. Sittiketkron and ***T. Bongkarn*** “Effect of Excess PbO on Crystal Structure, Microstructure and Phase Transition of Lead Titanate Ceramics” Smart/Intelligent Materials and Nano Technology 2008 (SmartMat-08), Chiang Mai, THAILAND (2008).

32. ***T. Bongkarn*** and R. Sumang “The Effect of Excess PbO on Crystal Structure and Microstructure of $(Pb_{0.925}Ba_{0.075})TiO_3$ Ceramics” Smart/Intelligent Materials and Nano Technology 2008 (SmartMat-08), Chiang Mai, THAILAND (2008).

33. ***T. Bongkarn*** and C. Wicheanrat “The Preparation of Barium Strontium Titanate Ceramics via Combustion Method” Smart/Intelligent Materials and Nano Technology 2008 (SmartMat-08), Chiang Mai, THAILAND (2008).

34. ***T. Bongkarn*** and W. Khiawwangthong “The Preparation of Barium Stannate Titanate Ceramics via Solid State Reaction Method” Smart/Intelligent Materials and Nano Technology 2008 (SmartMat-08), Chiang Mai, THAILAND (2008).

Executive Summary

เลดเซอร์โคเนต ($PbZrO_3$) เป็นวัสดุแอนติเฟร์โรอิเล็กทริก ซึ่งที่อุณหภูมิห้องจะมีโครงสร้างเป็นแบบออโธรอมบิก โดยมีการเปลี่ยนเฟสจากออโธรอมบิกสู่คิวบิกที่อุณหภูมิประมาณ 236 ^{o}C อย่างไรก็ตามถ้าสารตั้งต้นมีความบริสุทธิ์เพียงพอ จะทำให้เกิดเฟสรอมโบฮีดรอลขึ้นระหว่างเฟสออโธรอมบิกและเฟสคิวบิก ที่อุณหภูมิประมาณ 230 ^{o}C การเปลี่ยนเฟสจากออโธรอมบิกสู่เฟสรอมโบฮีดรอลนี้จะทำให้เซรามิกเลดเซอร์โคเนตเกิดการขยายตัวอย่างมาก ($\sim$ 0.8%) ทำให้เซรามิกชนิดนี้มีความเหมาะสมในการประยุกต์ทำเป็นตัวขับเร้า (actuator) หรือ ตัวกักเก็บพลังงาน (energy storage)

นอกจากการใช้สารตั้งต้นที่มีความบริสุทธิ์แล้ว การแทนที่อะตอมของตะกั่วด้วยแบเรียม ก็จะทำให้เกิดเฟสรอมโบฮีดรอลระหว่างเฟสออโธรอมบิกและเฟสคิวบิกได้เช่นกัน และยังพบอีกว่าเมื่อปริมาณแบเรียมเพิ่มขึ้นจะทำให้อุณหภูมิคูรีลดลง และช่วงอุณหภูมิของเฟสรอมโบฮีดรอลเพิ่มมากขึ้น การเติมแบเรียมในปริมาณที่เหมาะสม (10 %) จะทำให้การขยายตัวที่เกิดขึ้นจากการเปลี่ยนเฟสออโธรอมบิกเป็นเฟสรอมโบฮีดรอล มีค่าสูงถึง $\sim$ 1% จึงทำให้เลดแบเรียมเซอร์โคเนตมีความเหมาะสมอย่างมากที่จะนำไปประยุกต์เป็นอุปกรณ์ไฟฟ้าดังได้กล่าวแล้ว

อย่างไรก็ตามการเปลี่ยนแปลงเฟสจากออโธรอมบิกเป็นรอมโบฮีดรอล ของเซรามิกเลดแบเรียมเซอร์โคเนตจะพบเฉพาะเซรามิกที่ได้จากการเตรียมด้วยวิธีทางเคมี ซึ่งเป็นวิธีที่มีความซับซ้อน ต้องอาศัยทักษะ และความชำนาญ นอกจากนี้ยังเตรียมสารได้ในปริมาณน้อย และมีค่าใช้จ่ายสูง ทำให้ไม่เหมาะสมในการนำไปใช้ในเชิงพาณิชย์ ในขณะที่การเตรียมสารด้วยวิธีมิกซ์ออกไซด์ เป็นวิธีที่มีความสะดวก ไม่ยุ่งยาก เตรียมสารได้ในปริมาณครั้งละมากๆ และต้นทุนต่ำ แต่ต้องใช้อุณหภูมิในการเผาสารที่สูงกว่าการเตรียมด้วยวิธีทางเคมี ซึ่งทำให้เกิดการระเหยของตะกั่วในปริมาณมาก เป็นเหตุให้องค์ประกอบของเซรามิกเปลี่ยนไป จนไม่สามารถพบการเปลี่ยนแปลงเฟสระหว่างออโธรอมบิกเป็นรอมโบฮีดรอลได้

ถ้าหากเราเติมปริมาณตะกั่วส่วนเกินเพื่อเป็นสารตั้งต้นในปริมาณที่เหมาะสม ก็จะทำให้เราได้เซรามิกเลดแบเรียมเซอร์โคเนตตามต้องการได้นอกจากนี้งานวิจัยในอดีตที่ผ่านมา สมบัติทางกายภาพ โครงสร้างเฟส สมบัติทางไฟฟ้า สมบติทางความร้อน สมบัติจุลภาค และสมบัติเชิงกลของเซรามิกเลดเซอร์โคเนต ซึ่งมีความสำคัญในการออกแบบเพื่อประยุกต์ทำเป็นตัวขับเร้า และตัวกักเก็บพลังงาน ยังไม่มีผู้วิจัยและรายงานผล และเพื่อเป็นการสร้างองค์ความรู้ใหม่ รวมทั้งหาแนวทางประยุกต์ใช้เซรามิกเลดแบเรียมเซอร์โคเนตในเชิงอุตสาหกรรม ทำให้การวิจัยนี้มุ่งความสนใจไปที่ผลปริมาณตะกั่วส่วนเกินที่มีต่อสมบัติต่างๆของเซรามิกเลดแบเรียมเซอร์โคเนต ที่เตรียมโดยวิธีมิกซ์ออกไซด์

โดยมีวัตถุประสงค์เพื่อศึกษาปริมาณตะกั่วส่วนเกินที่เหมาะสมในการเตรียมผงและเซรามิกของเลดแบเรียมเซอร์โคเนต ด้วยวิธีมิกซ์ออกไซด์ เพื่อศึกษาผลของปริมาณตะกั่วส่วนเกินที่มีต่อสมบัติทางกาย โครงสร้างเฟส สมบัติทางไฟฟ้า สมบัติทางความร้อน สมบัติทางจุลภาค และสมบัติเชิงกล ของเซรามิกเลดแบเรียมเซอร์โคเนต เพื่อสร้างองค์ความรู้ใหม่ และหาแนวทางในการ

ประยุกต์ใช้เซรามิกเลดแบเรียมเซอร์โคเนตในเชิงอุตสาหกรรม เพื่อสร้างนักวิจัยรุ่นใหม่ และสร้างผลงานวิจัยระดับนานาชาติ

เริ่มจากการเตรียมผงผลึกเลดแบเรียมเซอร์โคเนตที่มีปริมาณแบเรียมและตะกั่วส่วนเกินเป็นสารตั้งต้นที่ต่างๆ กัน ด้วยวิธีมิกซ์ออกไซด์ จากนั้นนำผงผลึกเลดแบเรียมเซอร์โคเนตที่ได้ไปเผาซินเตอร์ แล้วไปทำการศึกษาผลของปริมาณตะกั่วส่วนเกิน ที่มีต่อสมบัติทางกายภาพ โครงสร้างเฟส สมบัติทางไฟฟ้า สมบัติทางความร้อน สมบัติทางจุลภาค และสมบัติเชิงกล ของเซรามิกเลดแบเรียมเซอร์โคเนต แล้วนำผลที่ได้จากการวิเคราะห์มาเปรียบเทียบกับงานวิจัยในอดีตที่ผ่านมา สรุปผลและนำเสนอผลงานในวารสารวิชาการระดับนานาชาติ

สารบัญ

Phase transition, dielectric and piezoelectric properties of perovskite $(Pb_{1-x}Ba_x)ZrO_3$ ceramics

Abstract

$(Pb_{1-x}Ba_x)ZrO_3$ ceramics were prepared in the composition range $0.00 \leq x \leq 0.30$ by the mixed oxide solid state reaction method. The samples were kept at the calcination temperature 1000°C for 1 h and at the sintering temperature 1300 °C for 3 h. The structural phase transitions and the dielectric properties were studied. It was found that the density of the ceramics decreases with increasing amount of Ba^{2+}, whilst the average grain size is in the range 1 - 2.3 μm. The structure of as-calcined powder reveals that the fraction of the orthorhombic phase is decreasing with increasing Ba^{2+} content. The values of Vickers and Knoop hardness are in the range of 4-6.48 and 4.15–5.67 GPa, respectively. Dielectric measurements show that the AFE-FE and the FE-PE phase transformation temperatures decrease with increasing Ba^{2+} concentration. The AFE-FE phase transformation is detected for compositions $0.00 \leq x \leq 0.075$. The maximum dielectric constant gradually increases with increasing composition up to $x = 0.20$. For higher Ba^{2+} concentrations, the lowering of the maximum dielectric value is accompanied by a progressive broadening of the permittivity peak. The d_{33} values of the samples increase from ~ 0 to 87 pC/N with increasing Ba2+ concentration from x = 0.00 to 0.30 .

1. INTRODUCTION

Lead Zirconate, $PbZrO_3$ (PZ), is one end member of the industrially interesting solid-solution series $PbZrO_3$-$PbTiO_3$ [1] and the first antiferroelectric identified by Sawaguchi *et al.* [2,3]. At room temperature PZ has an antiferroelectric phase (AFE) which has an orthorhombic structure [2]. It undergoes the AFE to a

paraelectric phase (PE) and transforms from an orthorhombic structure to a cubic structure at 236^{o}C [4]. It is reported that there exists a ferroelectric phase (FE) over a very narrow temperature range (230-233 ^{o}C) [5-8]. The FE intermediate phase can also be introduced by partial replacement of Pb^{2+} ions with Ba^{2+} ions. The temperature range of this intermediate phase also increases with Ba concentration [9-16]. The AFE-FE phase transition produced a large volume expansion. It makes this material potentially useful for high displacement electromechanical actuator applications [15,16].

The effect of Ba^{2+} ion substitution on the phase transformation behavior of PZ has been investigated by many authors [4,9-21]. The first one was Roberts but he did not get any evidence for the AFE to FE transformation [4]. Later, Shirane investigated the phase transformation behavior of $(Pb_{1-x}Ba_x)ZrO_3$ (PBZ) for $0 \leq x \leq 0.30$ and reported that the ferroelectric intermediate phase does not appear until the Ba^{2+} concentration exceeds the threshold value at about 5 mol% [9]. The temperature range of this intermediate phase increases with the Ba^{2+} concentration. On the contrary, Ujma *et al.* reported the FE phase existence in PBZ containing up to 5 mol% Ba^{2+}, with dielectric properties different from the previous papers [17]. Harrad *et al.* carried out a detailed Raman scattering study of phase transformations in PBZ ceramics and showed that the AFE phase persists up to a critical composition of $x = 0.175$ [18,19]. Recently, Pokharel *et al.* synthesized PBZ by a semiwet route to ensure a homogeneous distribution of Pb^{2+} and Ba^{2+}[14-17,20,22]. They found unusually wide thermal hysteresis in the transformation temperatures measured by dielectric measurement during heating and cooling cycles (e.g., nearly 100 ^{o}C for $x = 0.05$ in contrast to about 11 ^{o}C for pure PZ) and an irreversibility of the AFE to FE transformation temperature during the cooling cycle for $x = 0.10$.

However, the dielectric constant measured on the cooling cycle of PBZ ceramics prepared via the mixed oxide solid state method has not been performed. Moreover, microstructures, mechanical and piezoelectric properties of the PBZ system are not clearly understood. Therefore, in this present work, $(Pb_{1-x}Ba_x)ZrO_3$ (PBZ) for $0 \leq x \leq 0.30$ were prepared by the solid state reaction method. The structural phase, densification, microstructure, mechanical and piezoelectric properties of PBZ ceramics were investigated as a function of composition x. Permittivity measurements were also used to study the details of antiferroelectric (AFE) to ferroelectric (FE) and ferroelectric (FE) to paraelectric (PE) phase transformations accompanied with evaluations of the dielectric behaviors of the PBZ samples. The results were discussed and compared to previous work.

2. EXPERIMENTAL PROCEDURE

The $(Pb_{1-x}Ba_x)ZrO_3$, $0 \leq x \leq 0.30$, ceramics were prepared using a conventional mixed oxide method. The raw materials of PbO, ZrO_2 and $BaCO_3$ were weighed and mixed. Each mixture of the starting powders was milled and mixed in a ball mill, as well as wet-homogenized with acetone for 24 h using zirconia grinding media. The suspensions were dried and the powders were ground using an agate mortar and sieved into fine powder. All obtained powders were calcined at 1000 °C for 1 h. The calcined powders were reground by wet ball-milling with 1wt% binder (B-5 supplied by Rohn-Haas, Germany) for 24 h. The calcined powders with binder were dried, crushed, and sieved again. The powder mixtures were isostatically pressed at 80 MPa into a pellet of 15 mm in diameter.

Finally, the pellets were fired in an alumina crucible and sintered at 1300 °C for 3 h. In order to minimize the loss of lead due to vaporization, the PbO atmosphere for

the sintering was maintained using $PbZrO_3$ as the spacer powder. Thermogravimetric and differential thermal analysis (TG-DTA) techniques were used to monitor the thermal behavior due to the reactions between the oxide precursors carried out on the powder mixtures at a heating rate of 10 ^oC/min with a simultaneous thermal analyzer (PERKIN ELMER Model TGA-7 and DTA-7). The microstructures of the sintered samples were examined using a scanning electron microscopy (JEOL, JSM5910). The phase formation of the calcined powders was determined using a diffractometer (Philips ADP1700). The density of the sintered samples was measured by Archimedes' method with distilled water as the fluid medium. The effect of Ba^{2+} content on the mechanical properties of the ceramics was studied by Vickers and Knoop microhardness testers. Indentations were applied on the polished surfaces of PBZ ceramics. Applied loads were 500 and 50 g for Vickers and Knoop microhardness, respectively, with an indentation period of 15 s. The sintered samples were prepared for electrical property measurements by first polishing and then gold sputtering on to the clean pellet faces. Poling was done conventionally in a silicone oil bath at 170 °C with a field of 25 kV/cm. After poling, the d_{33} coefficient was measured using a d_{33} tester (Pennebaker Model 8000). The dielectric measurements were carried out at 1 kHz using a HIOKI 3532-50 impedance analyzer from room temperature to 300 °C with a heating and cooling rate of 0.5 °C/min controlled by a computer.

3. RESULTS AND DISCUSSION

The TG and DTA curves recorded at a heating rate of 10 ^oC/min in air for an equimolar mixture of lead oxide, barium carbonate and zirconium oxide where the ratio of Pb:Ba is 0.975:0.025 are given in Fig. 1. The TG curve shows two distinct weight losses. The first weight loss occur around 275 ^oC and the second one above

750 ^{o}C. The sample shows a small endothermic peak in the DTA curve ~ 100 ^{o}C. This DTA peak can be attributed to the vaporization of water. However, no anomaly was observed from the TG pattern at this temperature. This may indicate that the small amount of vaporization of water could not be detected by the TG measurement. The first weight loss relates to the elimination of the organic residual from the milling process [23]. After the first weight loss, the sample shows nearly zero weight loss up to 750 ^{o}C. Corresponding to the second fall in specimen weight, by increasing the temperature up to 700 ^{o}C, the solid-state reaction between PbO, $BaCO_3$ and ZrO_2 was observed. The broad endothermic characteristic in the DTA curve represents that reaction which has a minimum at 706 ^{o}C. Moreover, another endothermic peak with a minimum at 963 ^{o}C was also observed in this profile. Whist the DTA event at 522 ^{o}C is associated with the allotropic transition γ-$BaCO_3 \rightarrow \alpha$-$BaCO_3$, this kind of transition does not result in weight loss [24]. The result agreed with Gomez-Yanez *et al*., which analyzed the reaction of the milled powders of $BaCO_3$ and TiO_3 [25]. These data were used to make the decision of calcinations temperature at 1000 ^{o}C.

XRD patterns of the calcined $(Pb_{1-x}Ba_x)ZrO_3$ powders for $0.000 \leq x \leq 0.300$ are shown in Fig. 2. Other than the perovskite, the structural phase was not observed for the whole range of compositions. The result agreed with the TG and DTA results. Furthermore, the XRD patterns indicate that the replacement of Pb^{2+} by Ba^{2+} ions apparently influenced the orthorhombic $PbZrO_3$ structure. For all of the samples, the diffraction lines could be indexed with respect to an orthorhombic structure. The intensity ratio of 004/240 peaks and the relative intensity of superlattice reflections, namely 110 and 130/112 decreased with increasing Ba^{2+} content as shown in Fig. 3. Pokharel *et al.* reported that the XRD pattern of orthorhombic antiferroelectric (A_O) phase presents the doublet of 240 and 004 reflections which change to the single peak

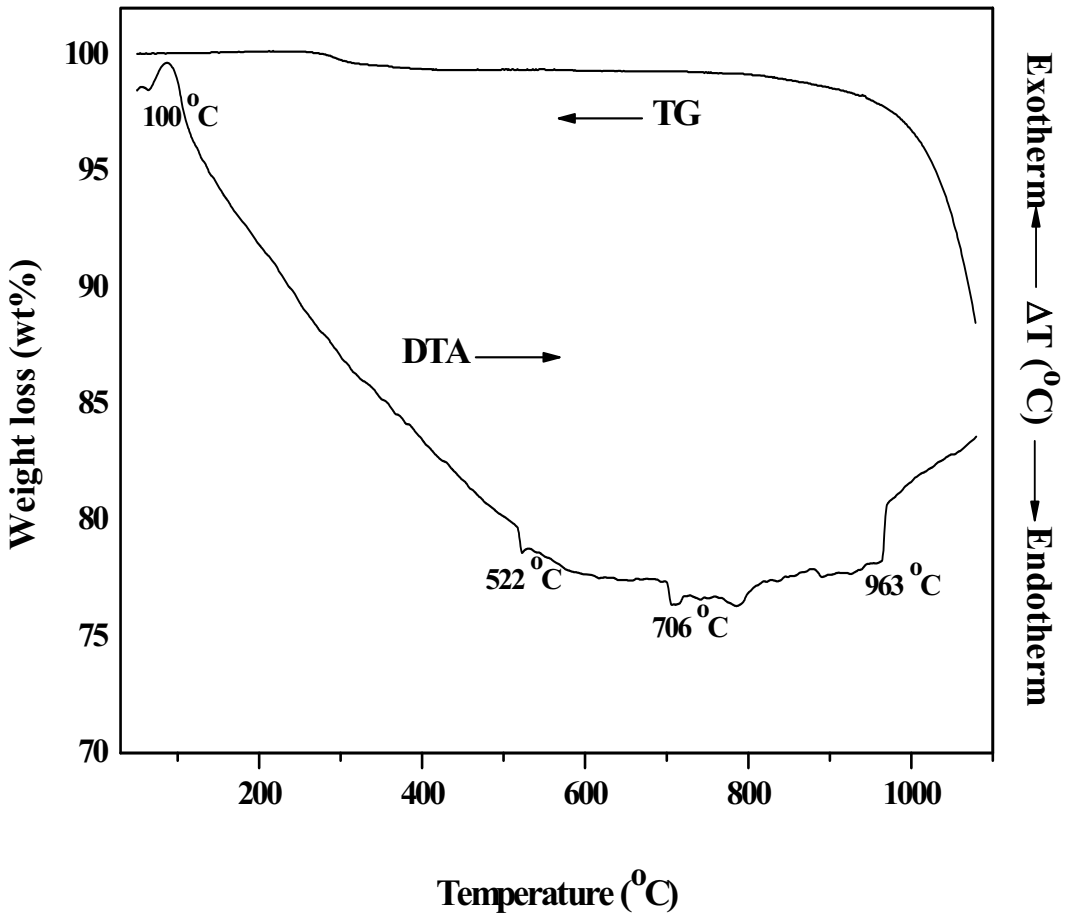


Fig. 1 TG and DTA curves for the mixture of PbO, BaCO3 and ZrO2 powders with the ratio of Pb:Ba = 0.975:0.025

of 200 reflections for the rhombohedral ferroelectric (F_R) phase [14-17]. For a purely orthorhombic pattern, the value $I_{004/240}$ ~0.5 decreases with increasing amounts of the coexisting rhombohedral phase. In addition, the superlattice reflections, such as 110 and 130/112 of A_O phase, disappear absolutely for the F_R phase. Futhermore, the structure of as-calcined powder also revealed that, the fraction of the orthorhombic phase decreases with increasing Ba^{2+} content.

Fig. 4 shows the typical sintered densities for various PBZ compositions. The bulk densities for all samples are higher than 97% of theoretical density. The bulk density continuously decreases with increasing Ba^{2+} content. The result agreed with

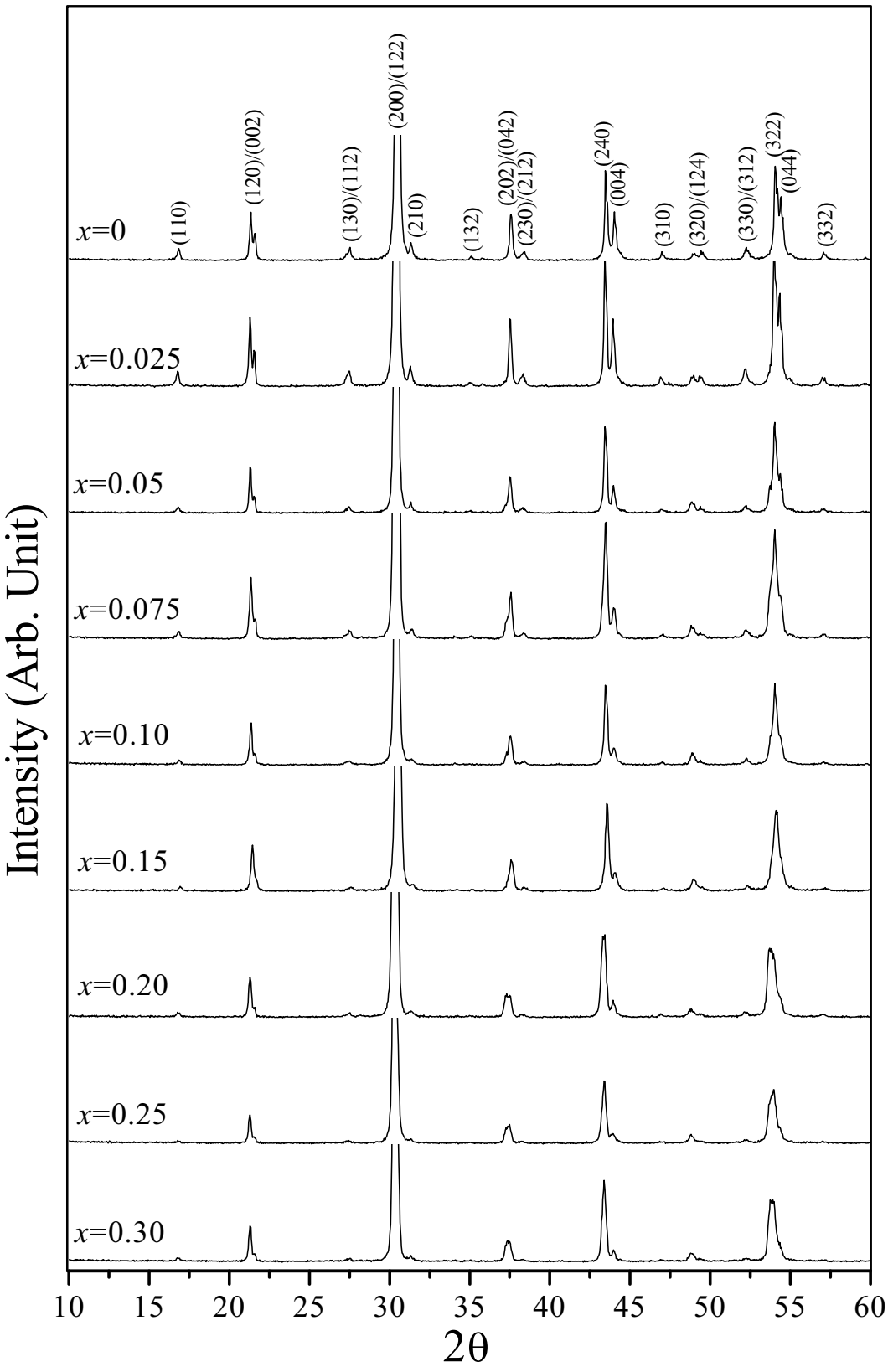


Fig. 2 XRD patterns of calcined powders of $(Pb_{1-x}Ba_x)ZrO_3$.

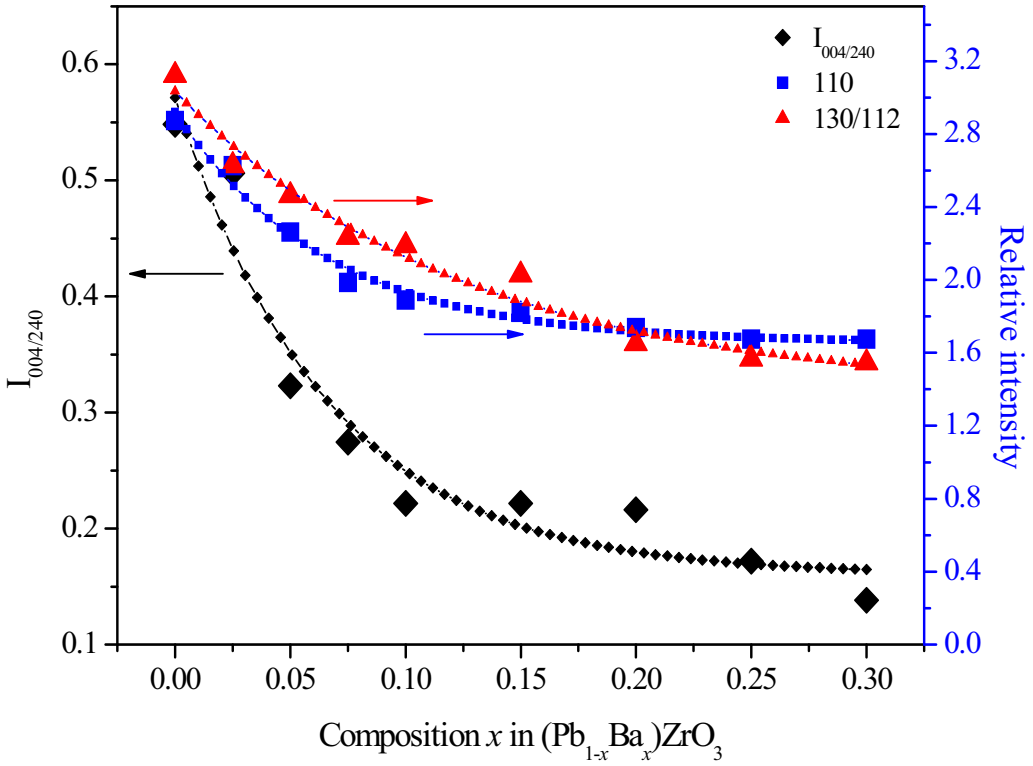


Fig. 3 Relative intensity of (110), (130)/(112) peaks and value of intensity ratio, $I_{004/240}$ as a function of Ba^{2+} content for calcined powders.

the work by Pokharel *et al.* [17]. In general, the bulk density of the $PbZrO_3$-$BaZrO_3$ system decreased with the increased mol percent of $BaZrO_3$ (BZ). The theoretical density of the constituent compounds PZ and BZ are 8.055 and 6.229 g/cm^3, respectively [26,27], which can be used to calculate an empirical estimate of the density (D) via the equation:

$$D = ((1-x)\times 8.055) + (x \times 6.229)$$

The variation of the measured density and the calculated density with composition x is also shown in Fig. 4.

The scanning electron micrographs in Fig. 5 show the as-sintered surface of $(Pb_{0.950}Ba_{0.050})ZrO_3$ and $(Pb_{0.800}Ba_{0.200})ZrO_3$ ceramics. It can be seen that the samples with higher Ba^{2+} concentration show more uniformity in grain size. The ceramics with

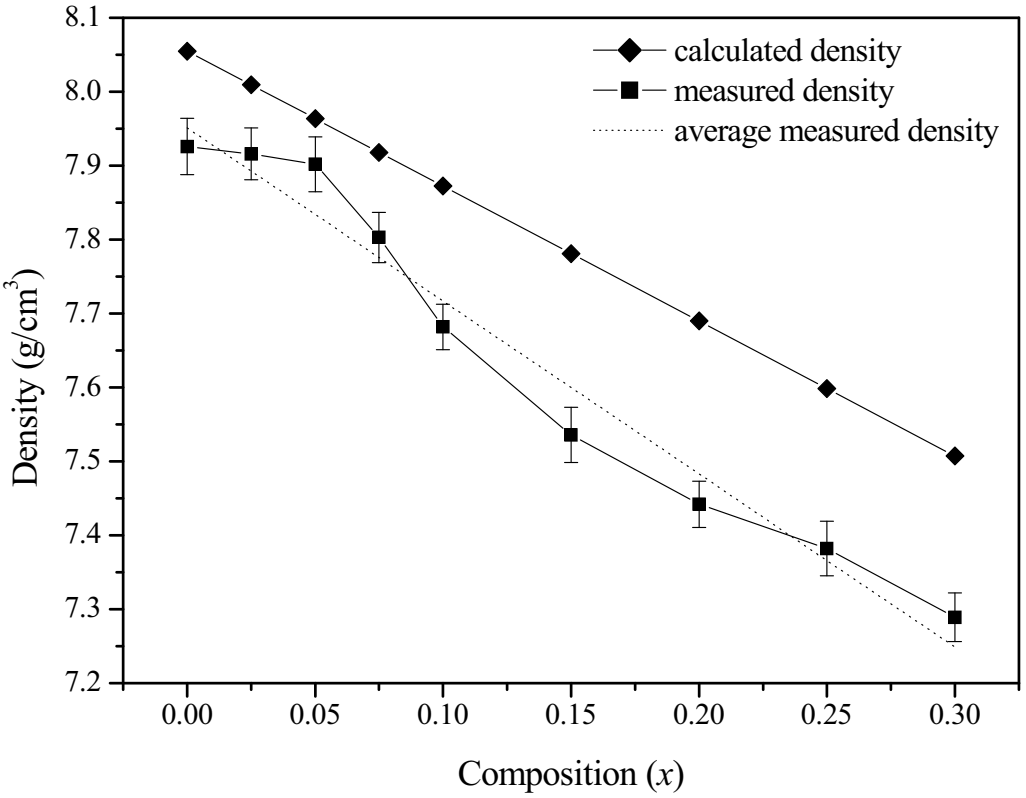


Fig. 4 Calculated density and bulk density of sintered pellets as a function of composition x.

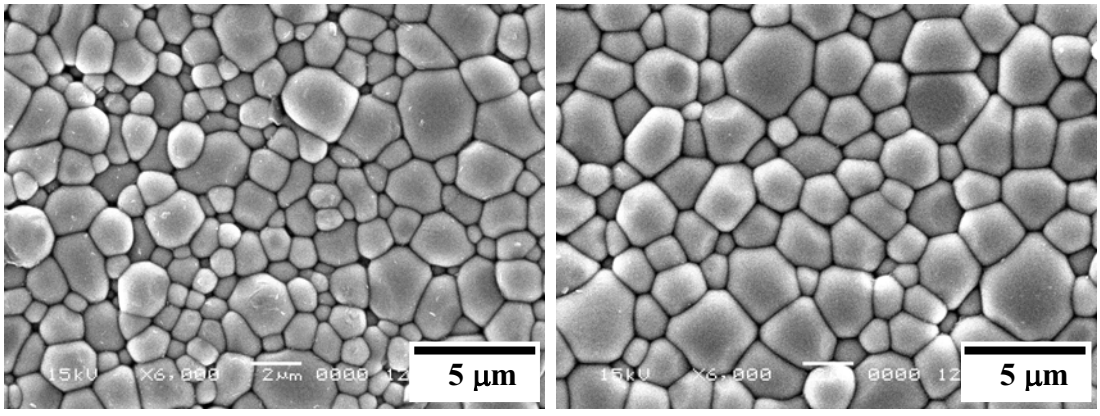


Fig. 5 SEM micrographs of as-sintered surface of (a) $(Pb_{0.950}Ba_{0.050})ZrO_3$ and (b) $(Pb_{0.800}Ba_{0.200})ZrO_3$ ceramics.

x = 0.000-0.050 compositions show a grain size of 1-1.3 μm, while the x = 0.075-0.300 compositions show a grain size of 1.7-2.3 μm (as seen in Table I). The effect of Ba^{2+} substitution on the mechanical properties of the samples was studied by using Vickers hardness, Knoop hardness fracture toughness, and Young's modulus. These values are also listed in Table I. It was found that there is no relation between Ba^{2+} concentration and the mechanical properties. Generally, the mechanical properties of lead base ceramics depend on many factors such as grain size and porosity [28]. The variation in mechanical properties is likely caused by the variation in grain size of the samples. Because the samples were prepared by normal solid-state method, the variation in mechanical properties may also be attributed to a chemical homogeneity effect.

Table I Average grain size and mechanical properties of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics.

Samples composition (x)	Average Grain size (μm)	Vickers hardness (GPa)	Knoop hardness (GPa)	Fracture toughness (MPa $m^{1/2}$)	Young's modulus (GPa)
0.000	1.0	4.81 ± 0.18	4.48 ± 0.48	3.30 ± 0.19	445 ± 55.06
0.025	1.3	6.48 ± 0.44	4.21 ± 0.77	2.04 ± 0.32	183 ± 39.76
0.050	1.3	5.83 ± 0.32	4.79 ± 0.37	1.84 ± 0.25	144 ± 41.63
0.075	2.3	5.61 ± 0.49	4.68 ± 0.35	2.15 ± 0.95	287 ± 151.26
0.100	1.6	5.85 ± 0.35	4.50 ± 0.33	1.57 ± 0.59	167 ± 116.26
0.150	2.0	5.10 ± 0.58	5.72 ± 0.31	2.75 ± 1.19	244 ± 152.60
0.200	1.7	4.61 ± 0.65	4.43 ± 0.26	2.60 ± 0.68	231 ± 87.24
0.250	1.7	5.30 ± 0.59	5.19 ± 0.53	2.25 ± 0.40	308 ± 94.04
0.300	2.2	4.10 ± 0.60	4.79 ± 0.37	2.54 ± 0.54	185 ± 74.95

Fig. 6 depicts the variation of the dielectric constant with different temperatures during heating and cooling of samples for $0 \leq x \leq 0.30$. By replacing

lead with barium, the dielectric maximum of lead zirconate is shown to shift to a lower temperature. Anomalies around 193, 157, and 116 °C for x = 0.025, 0.050 and 0.075, respectively, on heating were found. These anomalies are due to transformation from the A_O phase to F_R phase [9,13,29] while the maximum dielectric on heating in all samples, is linked with the transformation of the F_R phase into the cubic paraelectric (P_C) phase [9,13,29].

The AFE to FE transformation of PZ has not been observed during heating, as can be seen Fig. 6. The absence of phase transformation may be due to some impurities from raw materials [6,30]. The FE to AFE transformation during cooling occurs at 194 °C. The intermediate FE phase of PZ exists only on the cooling cycle which agrees with previous work [31-33]. However, the FE to AFE transformation temperature in this study is lower than in the former study. The reason for the lower FE to AFE transformation temperature of PZ is as yet unknown.

Furthermore, the AFE to FE transformation of PBZ7.5 is observed only during the heating cycle. Whist on the cooling cycle, the FE to AFE transformation of PBZ7.5 was not observed even when investigated from dielectric loss measurement. This result is similar to what has been reported by Pokharel *et al.*, in the dielectric measurement for $(Pb_{0.90}Ba_{0.10})ZrO_3$ [14,15]. It has been proposed that the occurrence of a AFE to FE on heating, but no reverse cooling transition, is because the transformation is subject to a large temperature hysteresis, shifting the FE phase transition to below room temperature on the cooling cycle [15]. An alternative explanation is that the FE to AFE phase transition is sluggish and the FE phase is quenched to room temperature [14]. It has also been reported that the AFE phase can reappear after long-term (several months) aging [14]. In the present work, the thermal hysteresis of the AFE↔FE phase transformation is about 80 and 100 ^{o}C for

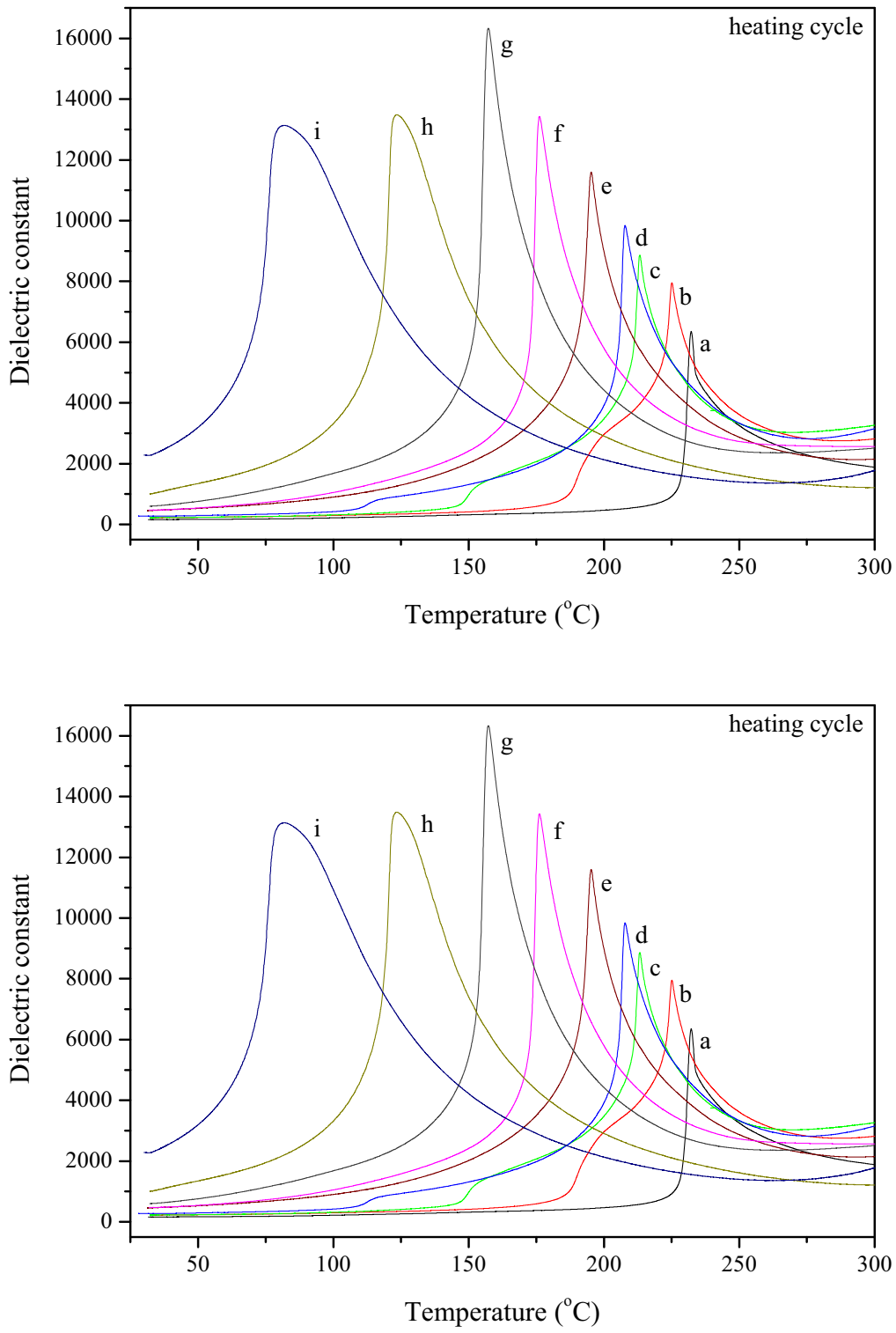


Fig. 6 Dielectric constant versus temperature on heating and cooling cycle of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics; (a) x=0, (b) x=0.025, (c) x=0.05, (d) x=0.075, (e) x=0.10, (f) x=0.15, (g) x=0.20, (h) x=0.25, (i) x=0.30.

compositions of x = 0.025 and 0.050, respectively. The width of the temperature range of F_R phase on heating is 32.6, 56.7 and 92.3 ^oC for the compositions of x = 0.025, 0.050 and 0.075, respectively, while on cooling it is 35.5, 110.0 and 143.3 ^oC for the compositions of x = 0.00, 0.025 and 0.050, respectively, (Fig. 7). It can be noted that the AFE to FE transformation temperature decreases nearly linearly at the rate of ~ 16 °C/mol% of $BaZrO_3$ with respect to its value for pure PZ.

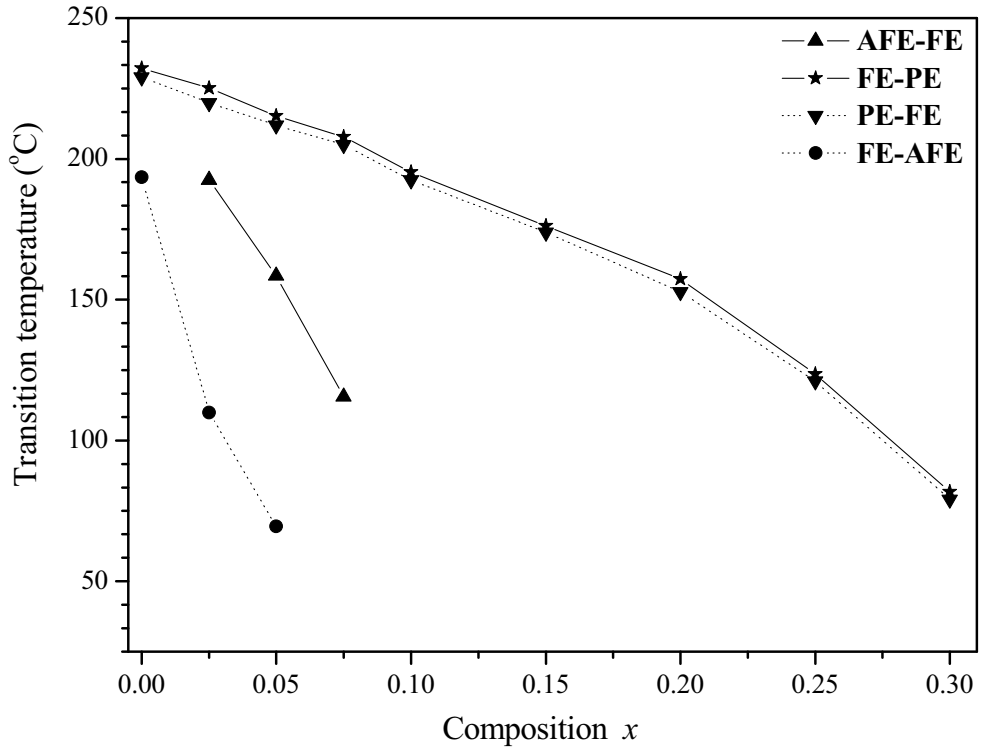


Fig. 7 Transition temperature as a function of composition x at 1 kHz

The increase in the amount of Ba^{2+} is accompanied by a decrease in the Curie transformation temperature. Barium substitution at the Pb^{2+} site increases the room temperature dielectric constant from 160 for pure PZ to nearly 2300 for PBZ30 while the maximum dielectric constant at Curie point during the heating cycle increases with increasing Ba^{2+} content from 6300 for pure PZ to 16300 for PBZ20 (x = 0.20). For higher Ba^{2+} concentration, the lowering of maximum dielectric values is

accompanied by progressive broadening of the permittivity peak. As shown in Fig. 7, the Curie temperature shifted to a lower temperature linearly, which may be explained by the increase of symmetry in PBZ structure with increasingly larger Ba^{2+} ions with Pb^{2+} site, and this system is a well behaved complete solid solution. These results are similar to those reported in earlier papers [9,13]. However, in this study, the specimens exhibited a higher dielectric constant than earlier papers [4,9,14,15], probably due to better conditions for the sinter process. Hence, dense and homogeneous samples were achieved. The difference in the transformation temperatures obtained during heating and cooling measurements in all samples was around 3 °C confirming that the FE to PE transformation over the entire composition range ($0 < x < 0.30$) is first order [6,8,15].

The longitudinal piezoelectric sensitivity of $(Pb_{1-x}Ba_x)ZrO_3$ at room temperature is shown in Fig. 8. The d_{33} value gradually increases with increasing

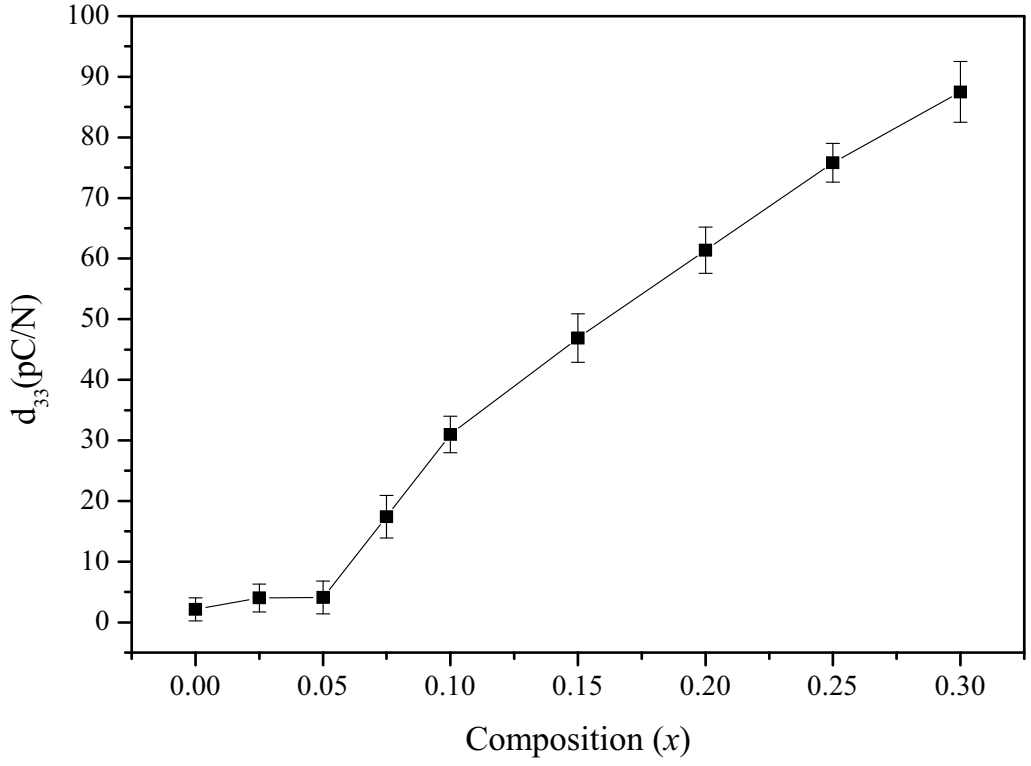


Fig. 8 Piezoelectric coefficient d_{33} and dielectric constant at room temperature of $(Pb_{1-x}Ba_x)ZrO_3$ with various x.

Ba^{2+} content. Roberts [4] reported that the d_{33} value of $(Pb_{0.700}Ba_{0.300})ZrO_3$ was ~ 65 pC/N, and it was 10^{-1} pC/N for PZ [34]. The present result indicated that substitution of Pb^{2+} by Ba^{2+} enhanced some piezoelectric properties in PBZ.

4. CONCLUSIONS

In the present work, the effect of Ba^{2+} concentration on the properties of the PBZ ceramics was studied. The orthorhombic phase and the fraction of the antiferroelectric phase were found to decrease with increasing Ba^{2+} content. The results corresponded to the structural phase changes in PBZ. The bulk density of PBZ ceramics continuously decreases with increasing Ba^{2+}content. This trend matches that of the calculated density of the PZ-BZ system. The d_{33} value at room temperature gradually increases with increasing Ba^{2+} content. Furthermore, the results indicated that Ba^{2+} concentration has a significant effect on the dielectric properties in PBZ ceramics. The AFE-FE and FE-PE phase transformation temperatures progressively decrease with continuously increasing Ba^{2+} concentration. The AFE-FE phase transformation was detected for compositions $0.00 \leq x \leq 0.075$. However, there is no relation between Ba^{2+} concentration and mechanical properties.

REFERENCE

[1] F.W. Ainger, Modern Oxide Materials, Academic Press, New York, 1972, P. 147-175.

[2] E. Sawaguchi, G. Shirane, S. Hoshino, *Phys. Rev.***83** (1951), P.1078.

[3]. E. Sawaguchi, G. Shirane, Y. Takagi, *J. Phys Jpn. Soc.* **6** (1951) P.333-339.

[4] S. Roberts, *J. Am. Ceram. Soc*. **33** (1953) P.63-66.

[5] L. Goulpeau, *Sov. Phys. Solid St.* **8** (1967) P.1970-1971.

[6] V.J. Tennery, *J. Am. Ceram. Soc.* **49** (1966) P.483-486.

[7] B.A. Scott, G. Burns, *J. Am. Ceram. Soc.* **55** (1972) P.331-333.

[8] R.W. Whatmore, A.M. Glazer, *J. Phys. C: Solid State Phys.* 12 (1979) P.1505-1516.

[9] G. Shirane, *Phys. Rev.* **86** (1952) P.219-227.

[10] G. Shirane, S. Hoshino, *Acta Cryst.* **7** (1954) P.203-210.

[11] K. Yamakawa, S. Trolier-McKinstry, J. P. Dougherty and S. B. Krupanidhi, *Appl. Phys. Lett.* **67**(14), 1995, P.2014-2016

[12] Z. Ujma, J. Handerak, M. Pawelczyk, D. Dmytrow, *Ferroelectrics* **129**(1992) P.127-139.

[13] K.H. Yoon, S.C. Hwang, *J. Mater. Sci.* **32** (1997) P.17-21.

[14] B.P. Pokharel, D. Pandey, *J. Appl. Phys.* **86** (1999) P.3327-3332.

[15] B.P. Pokharel, D. Pandey, *J. Appl. Phys.* **88** (2000) P.5364-5373.

[16] B.P. Pokharel, D. Pandey, *J. Appl. Phys.* **90** (2001) P.2985-2294.

[17] B. P. Pokharel, M. K. Datta, D. Pandey, *J. Mater. Sci.* **34** (1999) P.691-700.

[18] I. El-Harrad, P. Becker, C. Carabatos-Nedelec, J. Handerek, Z. Ujma, D. Dmytrow, *Vib. Spectrosc.* **10** (1996) P.301-309.

[19] I. El-Harrad, A. Ridah, C. Carabatos-Nedelec, P. Becker, J. Handerek, Z. Ujma, D. Dmytrow, *J. Raman Spectrosc.* **29** (1998) P.123-129.

[20] I. El-Harrad, A. Ridah, *Ferroelectrics* **265** (2002) P.211-223.

[21] B. P. Pokharel, R. Ranjan, D. Pandey, *Appl. Phys. Lett.* **74** (1999) P.756-758.

[22] B. P. Pokharel, D. Pandey, *Phys. Rev. B* **65** (2002) P.214108.

[23] J. Fang, J. Wang, L.M. Gan, S.C. Ng, *Mater. Lett*., **52** (2002) P 304.

[24] R.H. Perry, D. Green, Perry's Chemical Engineer's Handbook, McGraw Hill, Tokyo, 1984.

[25] C. Gomez-Yanez, C. Benitez, H. Balmori-Ramirez, *Ceram. Inter.*, **26** (2000) P 271.

[26] Powder Diffraction File no.87-0570, International Centre for Diffraction Data, Newton Square, PA, 2000.

[27] Powder Diffraction File no.06-0399, International Centre for Diffraction Data, Newton Square, PA, 2000.

[28] K. Uchino, Piezoelectric actuators/Ultrasonic motors, Kluwer Academic Publishers, London, 1996.

[29] A. P. Debretteville, *Phys. Rev.* **94** (1954) P.1125-1128.

[30] J. Handerek, M. Pawelczyk, Z. Ujma, *J. Phys. C* **14** (1981) P.2007-2016.

[31] D. F. Weirauch, V. J. Tennery, *J. Am. Ceram. Soc.* **53** (1970) P.229-232.

[32] Z. Ujma, J. Handerek, *J. Euro. Ceram. Soc.* **23** (2003) P.203-212.

[33] A. A. Belov, Y. Jeong, *J. Korean Phys. Soc.* **32** (1998) P.S299-S301.

[34] S. Roberts, *Phys. Rev.* **51** (1951) P.1078.

Phase transition and linear thermal expansion of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics

Abstract

$(Pb_{1-x}Ba_x)ZrO_3$ ceramics for the composition range $0 \leq x \leq 0.30$ were prepared by the mixed oxide solid state reaction method. Phase transition was studied by dielectric and dilatometric measurements. It was found that the ferroelectric to paraelectric phase transition temperatures progressively decrease with continuously increasing Ba^{2+} concentrations. The maximum dielectric constant gradually increases with increasing compositions x up to 0.20. For higher Ba^{2+} concentrations, the lowering of maximum dielectric values is accompanied by progressive broadening of the permittivity peak. For compositions $0 \leq x \leq 0.05$, the antiferroelectric to ferroelectric phase transition exhibited a large linear thermal expansion. This material has a potential for displacement electromechanical and thermal actuator applications.

1. Introduction

$PbZrO_3$ (PZ) is a perovskite crystal, which was identified as an antiferroelectric material. PZ exhibits three phases: an orthorhombic antiferroelectric (AFE) phase between room temperature and 230 ^oC, a rhombohedral ferroelectric (FE) phase up to 233 ^oC and a cubic paraelectric (PE) phase above 233 ^oC [1-5]. The ferroelectric phase between 230-233 ^oC is sometimes called the ferroelectric intermediate phase. The phase transitions between AFE to FE and FE to PE in PZ have been extensively studied by previous authors [4,5]. It is also reported that many properties of PZ are changed by incorporation of Ba^{2+} ions into the Pb^{2+} site of PZ [7-12]. The modification of PZ becomes $(Pb_{1-x}Ba_x)ZrO_3$ (PBZ) and exhibits the better dielectric properties compared with the pure PZ. By varying Ba^{2+} concentration,

electric field and temperature in PBZ, many phase diagrams have been proposed [8,9,12]. However, the information for thermal expansion associated with the phase transitions of the PBZ ceramics is unclear. In the present work, $(Pb_{1-x}Ba_x)ZrO_3$ ceramics for $0 \leq x \leq 0.30$ were prepared by the mixed oxide solid state reaction method. X-ray diffraction, dielectric and dilatometric techniques were used to study the details of the phase transitions.

2. Experimental procedure

It is reported that PBZ ceramics can be prepared by many methods [8,9,12]. However, in the present work, PBZ ceramics were prepared by a mixed oxide solid state reaction method as described by previous study [13]. The raw materials of PbO, ZrO_2 and $BaCO_3$ were weighed according to the formula $(Pb_{1-x}Ba_x)ZrO_3$, where $0 \leq x \leq 0.30$. The powders were mixed with acetone for 24 h using zirconia balls as the grinding media. The mixed powders were calcined at 1000 °C for 1 h. The calcined powders were reground by wet ball-milling with 1wt% binder for 24 h. The calcined powders with binder were isostatically pressed at 80 MPa into a pellet of 15 mm in diameter. Finally, the pellets were fired in an alumina crucible and sintered at 1300 °C for 3 h. It is reported that excess PbO affects on the properties of lead base ceramics [13,14]. There is a loss of lead due to varporization. In this experiment, the PbO atmosphere for the sintering was maintained using $PbZrO_3$ as the spacer powder. Phase formation of the samples was determined by X-ray diffraction (XRD). For electrical measurement, the sintered samples were polished and then gold was sputtered on to the clean pellet faces. The dielectric measurements were carried out at 1 kHz using an impedance analyzer, the linear thermal expansion was measured using a dilatometer.

3. Result and discussions

Figure 1 shows XRD patterns of $(Pb_{1-x}Ba_x)ZrO_3$ calcined powders. The XRD trace showed diffraction profiles as attributed to pure PBZ [7,10,11,14]. Due to peak overlap effects between rhombohedral and orthorhombic structures, the intensity of the peak indexed as 240 in the orthorhombic pattern increased relative to the neighbouring 004 peak with the presence of the rhombohedral phase [7,10,14]. These results indicate that the introduction of Ba^{2+} increases the proportion of the rhombohedral phase in PBZ calcined powders.

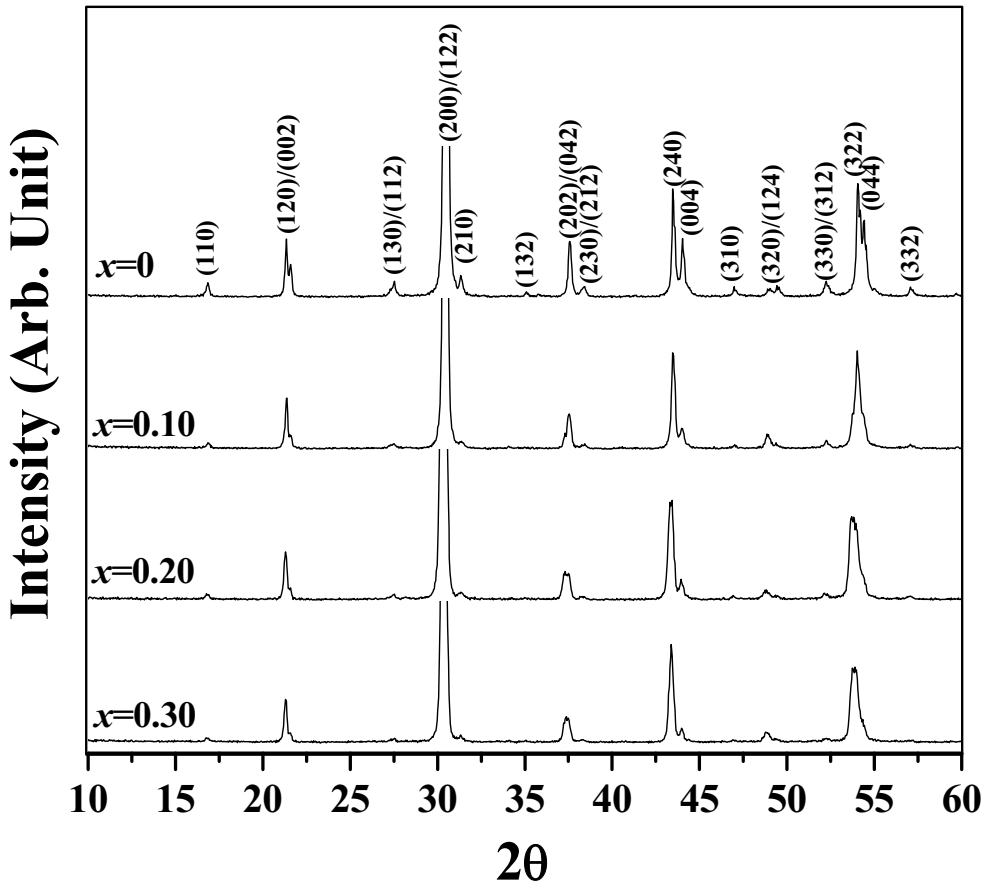


Fig.1 XRD patterns of calcined powders of $(Pb_{1-x}Ba_x)ZrO_3$.

XRD patterns of ceramic samples are shown in figure 2. The XRD patterns for composition of $0 \leq x \leq 0.10$ are qualitatively similar to that observed for the as-calcined powder. Although a similar situation prevails for the calcined powder, the sintered sample is predominantly rhombohedral whereas the calcined powder has a significant proportion of the orthorhombic phase as evidenced by the relative intensity of the 240 and 004 reflections. For composition $x = 0.15$, the XRD results indicated that both rhombohedral and orthombic phases coexisted. The rhombohedral 200 reflection, which was a doublet in the calcined powder, has become a single peak for composition $0.20 \leq x \leq 0.30$. This clearly indicates that the structure is rhombohedral for $0.20 \leq x \leq 0.30$ ceramic samples.

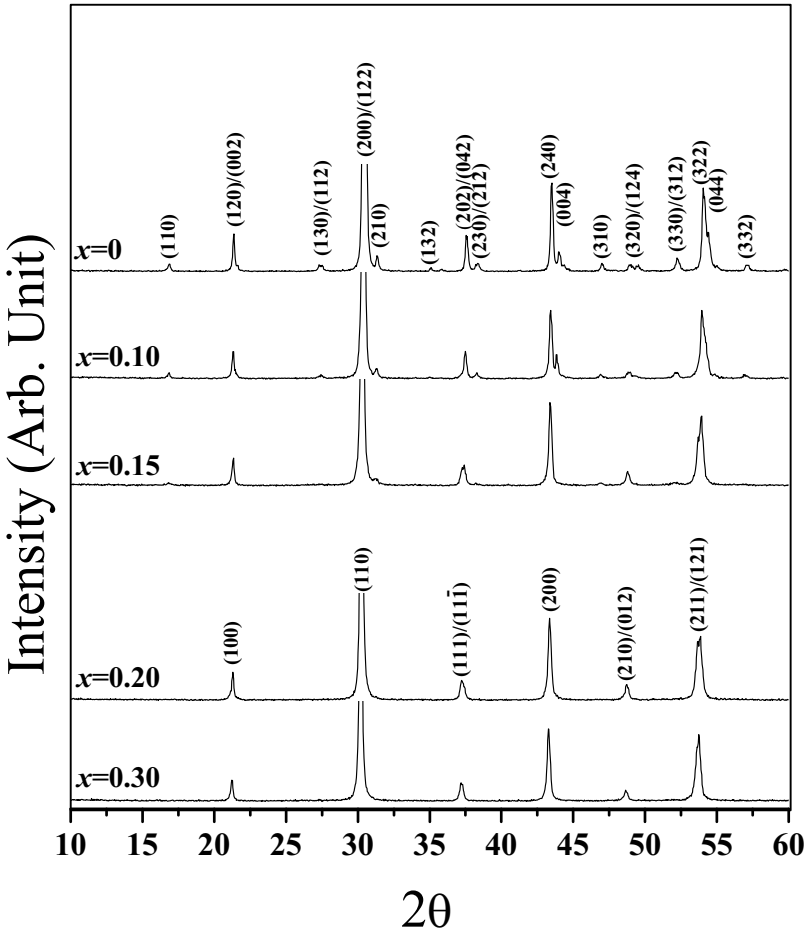


Fig.2 XRD patterns of as-sintered pellets of $(Pb_{1-x}Ba_x)ZrO_3$.

Figure 3 shows the variation of the dielectric constant with the temperature of samples for $0 \leq x \leq 0.30$. The dielectric maximum of lead zirconate is shown to shift to a lower temperature by replacing lead with barium, Fig.3. The dielectric maximum in all samples, is linked with the transition of the FE phase into the PE phase [9,10,12]. The transition temperature decreases at about the rate of 4.8 ^{o}C/mol% of $BaZrO_3$ with respect to its value for pure PZ. This transition temperature shifted to a lower temperature linearly which may be explained by the change of structure in PBZ with increasing Ba^{2+} ions as previously mentioned [7,9,11].

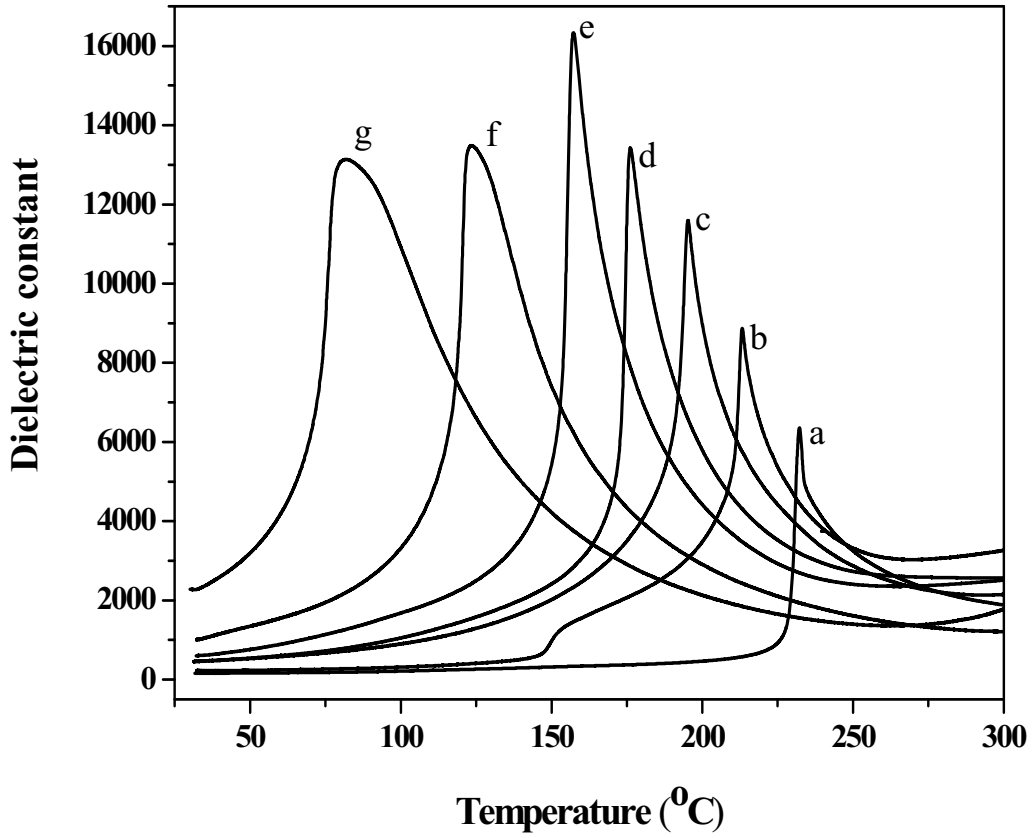


Fig. 3 Dielectric constant versus temperature of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics; (a) x=0, (b) x=0.05, (c) x=0.10, (d) x=0.15, (e) x=0.20, (f) x=0.25, (g) x=0.30.

The value of the maximum dielectric constant as a function of Ba^{2+} concentration is shown in figure 4. The maximum dielectric constant at the FE to PE phase transition temperature increases with increasing Ba^{2+} content from 6300 for pure PZ to 16300 for PBZ20 (x = 0.20). For higher Ba^{2+} concentration, the lowering of the maximum dielectric value is accompanied by progressive broadening of the permittivity peak. Barium substitution at the Pb^{2+} site also increases the room temperature dielectric constant from 160 for pure PZ to nearly 2300 for PBZ30. The change in the dielectric constant can be be related to the change of PBZ structure, i.e., the proportion of rhombohedral phase in PBZ increase with increasing Ba^{2+} content.

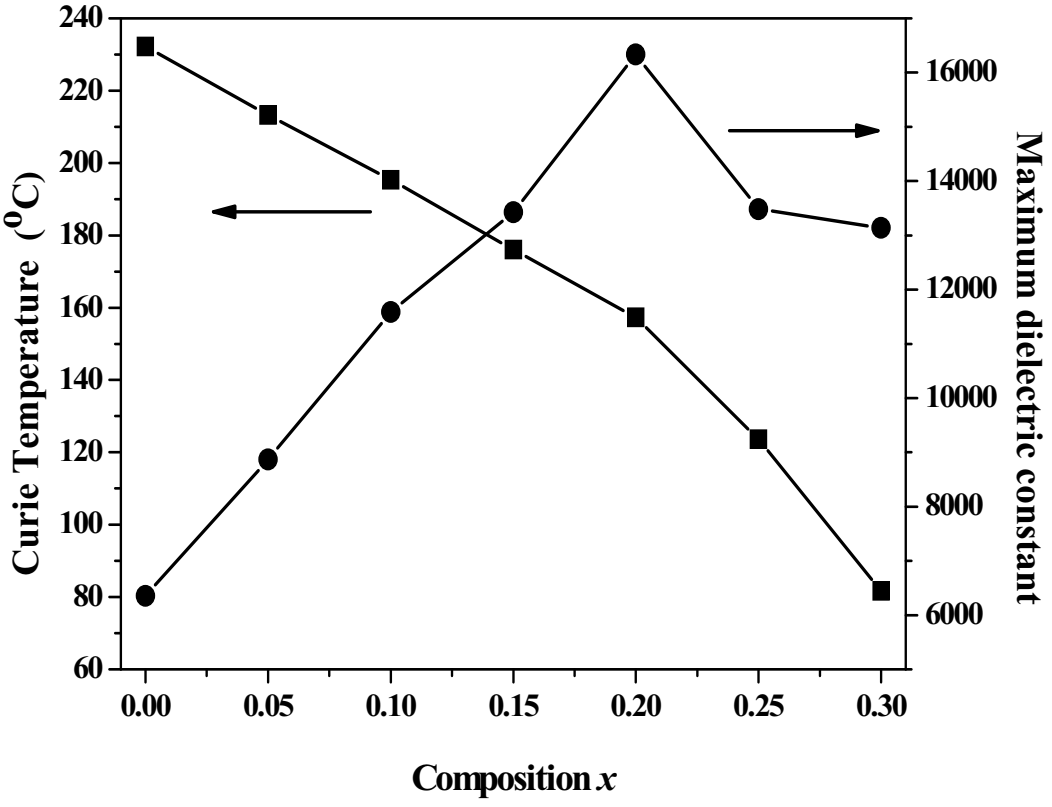


Fig. 4 Curie temperature and maximum dielectric constant of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics.

For the composition x = 0.05, anomaly around 157 ^{o}C was found. The jump in the dielectric curve at the transition temperature was found to be 1430. This anomaly is due to transition from the AFE to the FE phase [9,12]. The transition temperature closely agrees with literature values [9]. For $x \geq 0.10$, however, no AFE–FE transition is observed.

The measurement of the length of a specimen compared to its temperature is a method for the determination of the kinetics of the phase transformation of PBZ. The dilatometric thermal expansion of polycrystalline samples of $(Pb_{1-x}Ba_x)ZrO_3$, on heating is plotted in Fig. 4. The presence of such a break in the thermal expansion curves indicates a phase transition. The discontinuous curves are attributed to the AFE to FE and FE to PE phase transition with rising temperature [4,8]. For x=0 and 0.05 (PBZ5), the AFE-FE transformation was accompanied by a large expansion while the FE-PE transformation was accompanied by a small contraction. The linear thermal expansion due to the AFE-FE phase is 0.17 and 0.23 % for PZ and PBZ5, respectively. However, the AFE-FE phase transition could not be observed for compositions $0.10 \leq x \leq 0.30$. This indicates that the AFE phase trends to disappear for the compositions $x \geq 0.10$. This result is consistent with the dielectric result. For compositions $0.05 \leq x \leq 0.30$, the linear contraction due to FE-PE phase transition obviously continuously decreases with increasing Ba^{2+} content.

For PZ and modified PZ, the phase transition from AFE to FE can be induced by a high electric field, temperature or hydrostatic which is accompanied by a large volumetric change [9,15,16]. These characteristics of the PZ ceramic make it a candidate material for high displacement electromechanical actuator applications [10,15,16]. Furthermore, the large thermal expansion as observed in the present work indicates a potential for thermal actuator applications in this material.

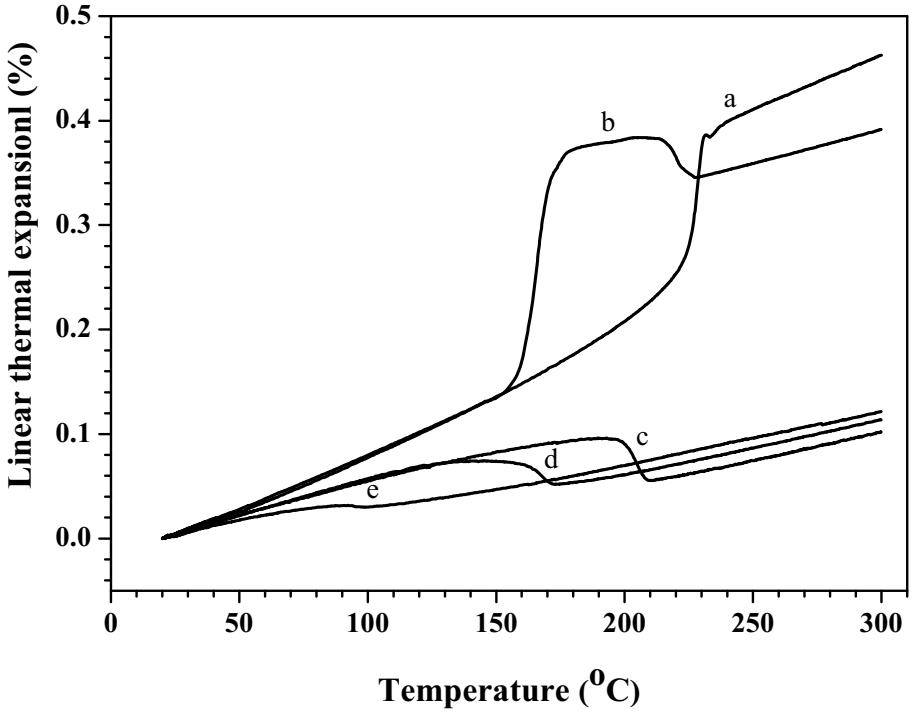


Fig. 5 Linear expansion versus temperature of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics; (a) x=0, (b) x=0.05, (c) x=0.10, (d) x=0.20 (e) x=0.30.

4. Conclusion

Based on dielectric measurements of PBZ which were prepared by a conventional method, the FE-PE phase transition temperatures progressively decrease with continuously increasing Ba^{2+} concentrations at the rate of 4.8 ^{o}C/mol% of $BaZrO_3$. The change in the dielectric curve can be associated with the structural change of PBZ as the Ba^{2+} content increases. From the dilatometric measurement, the AFE-FE phase transition of PZ and PBZ5 shows a large linear thermal expansion while FE-PE transformation for all compositions was accompanied by a small contraction. However, the AFE-FE phase transition was not observed for compositions $0.10 \leq x \leq 0.30$. This result is consistent with the dielectric measurement.

References

[1] S. Roberts, *J. Am. Ceram. Soc.*, 1950, 33 : 63.

[2] L. Goulpeau, Sov. *Phys. Solid St*., 1967, 8 : 1970.

[3] V. J. Tennery, *J. Am. Ceram. Soc.*, 1966, 49 : 483.

[4] B. A. Scott and G. Burns, *J. Am. Ceram. Soc.*, 1972, 55 : 331.

[5] R.W. Whatmore and A.M. Glazer, *J. Phys. C: Solid State Phys.*, 1979, 12 : 1505.

[6] G. Shirane and S. Hoshino, *Acta Crystallogr.*, 1954, 7 : 203.

[7] B. P. Pokharel, M. K. Datta, and D. Pandey, *J. Mater. Sci.*, 1999, 34 : 691.

[8] G. Shirane, *Phys. Rev.*, 1952, 86 : 219.

[9] K. H. Yoon, S. C. Hwang, and D. H. Kang, *J. Mater. Sci.*, 1997, 32 : 17.

[10] B. P. Pokharel and D. Pandey, *J. Appl. Phys.*, 1999, 86 : 3327.

[11] B. P. Pokharel and D. Pandey, *J. Appl. Phys.*, 2001, 90 : 2985.

[12] B. P. Pokharel and D. Pandey, *J. Appl. Phys.*, 2000, 88 : 5364.

[13] T. Bongkarn and G. Rujijanagul, *Curr. Appl. Phys.*, *(In Press)*.

[14] T. Bongkarn, G. Rujijanagul and S. J. Milne, *Mater. Lett.*, 2005, 59 : 1200.

[15] W. Y. Pan, Q. Zhang, A. Bhalla, and L. E. Cross, *J. Am. Ceram. Soc.*, 1989, 72 : 570.

[16] S-E. Park, M-J. Pan, K. Markowski, S. Yoshikaw, and L. E. Cross, *J. Appl. Phys.*, 1997, 82 : 1798.

Effect of Barium Substitution on Phase Transitions of Lead Barium Zirconium Ceramics Prepared by Solid State Reaction Method

Abstract

The effect of Ba^{2+} substitution on the phase transitions of $(Pb_{1-x}Ba_x)ZrO_3$ (PBZ) ceramics ($0.0 \leq x \leq 0.30$) has been investigated as a function of x. Phase formation and phase transition of PBZ were investigated by x-ray diffraction (XRD) and thermal analysis, respectively. It was found that the structure of sintered pellets is orthorhombic for $0.0 \leq x \leq 0.10$ and rhombohedral for $0.20 \leq x \leq 0.30$, whereas orthorhombic and rhombohedral phases coexist at $x = 0.15$. The proportion of ferroelectric and paraelectric phase in the samples gradually decreased with increasing Ba^{2+} content.

1. Introduction

Substitution of Ba^{2+} for Pb^{2+} in $PbZrO_3$(PZ) is of considerable interest for transducer applications since its volume change associated with field forced antiferroelectric (AFE) to ferroelectric (FE) transition increases with Ba^{2+} substitution [1,2]. Also, the longitudinal strain associated with the AFE to FE transition in these materials can be as large as 0.85%. This makes PBZ ceramic an interesting material for high displacement electromechanical actuator applications [3]. Thus, many authors have extensively studied the phase transitions behavior of PBZ [1-3,4-11]. The first one was Roberts who found no evidence of AFE $\rightarrow$ FE phase transition [6]. Later, Shirane investigated the phase transformation behavior of $(Pb_{1-x}Ba_x)ZrO_3$ for $0 \leq x \leq 0.30$ and reported that the ferroelectric intermediate phase does not appear until

the Ba^{2+} concentration exceeds the threshold value at about 5 mol% [1]. The temperature range of this intermediate phase increases with the Ba^{2+} concentration. However, Ujma *et al.* reported the FE phase existence in PBZ containing up to 5 mol% Ba^{2+}, with dielectric properties different from the previous works [7]. Recently, Pokharel *et al.* found unusually wide thermal hysteresis in the AFE$\leftrightarrow$FE phase transition, measured by dielectric measurement during heating and cooling cycles and an irreversibility of the FE to AFE(FE$\rightarrow$ AFE) phase transition during the cooling cycle for x = 0.10 [8]. It was suggested that the processing method used to prepare the PBZ may be important in influencing phase formation [10]. Thus, different research groups reported the different results of AFE$\leftrightarrow$FE phase transition. Ujma *et al.* suggested thermal analysis such as differential scanning calorimeter (DSC) is a good method for measuring the small anomaly of AFE$\leftrightarrow$FE phase transition [12]. Furthermore, the enthalpy associated with the phase transitions has not been widely investigated for this material. In this work, the PBZ ceramics were prepared by a solid-state method. DSC was used to study the details of AFE$\rightarrow$FE and FE$\rightarrow$PE phase transitions in PBZ ceramics. Structural phase formation of the ceramics was also investigated as a function of compositions x.

2. Experimental

The $(Pb_{1-x}Ba_x)ZrO_3$, $0 \leq x \leq 0.30$, ceramics were prepared by using a solid state method. Raw materials of PbO, ZrO_2 and $BaCO_3$ were weighed and mixed. Each mixture of the starting powders was milled and mixed in a ball mill, as well as wet-homogenized with acetone for 24 h using zirconia grinding media. The suspensions were dried and calcined at 1000 °C for 1 h. The calcined powders were reground by wet ball-milling with 1wt% binder for 24 h. The calcined powders with binder were

dried, crushed and sieved again. The powder mixtures were isostatically pressed at 80 MPa into a pellet of 15 mm in diameter. Finally, the pellets were sintered in an alumina crucible at 1300 °C for 3 h. In order to minimize the loss of lead due to vaporization, the PbO atmosphere for the sintering was maintained using $PbZrO_3$ as the spacer powder. The phase formation of the sintered pellets was determined by X-ray diffraction (XRD). The phase transition temperatures and enthalpy (ΔH) of the phase transitions were determined by DSC. This was operated from room temperature to 250 °C with a heating rate of 10 °C/min.

3. Results and discussion

Fig. 1 shows XRD patterns of $(Pb_{1-x}Ba_x)ZrO_3$ sintered pellets for $0.00 \leq x \leq 0.30$. Other than the perovskite, phase was not observed for the whole range of compositions. It was found that the lower barium content leads to the orthorhombic antiferroelectric (A_O) phase while higher barium content stabilizes the rhombohedral ferroelectric (F_R) phase. The diffraction lines for composition of $0.00 \leq x \leq 0.10$ could be indexed with respect to an orthorhombic structure and the fraction of the orthorhombic phase decreases with increasing Ba^{2+} content. These natures of XRD patterns are qualitatively similar to that observed for the as-calcined powder. For x = 0.15, the 004 reflection of the A_O phase has completely vanished as expected for F_R phase, but some of the superlattice reflections are still present. Pokharel *et al.* reported that the XRD pattern of A_O phase presents the doublet of 240 and 004 reflections change to the single peak of 200 reflections for F_R phase [4,8-10]. In addition, the superlattice reflections, namely 110, 130/112, 120 and 230/212 of A_O phase, are absolutely disappeared for the F_R phase. In present work, the results indicate that both

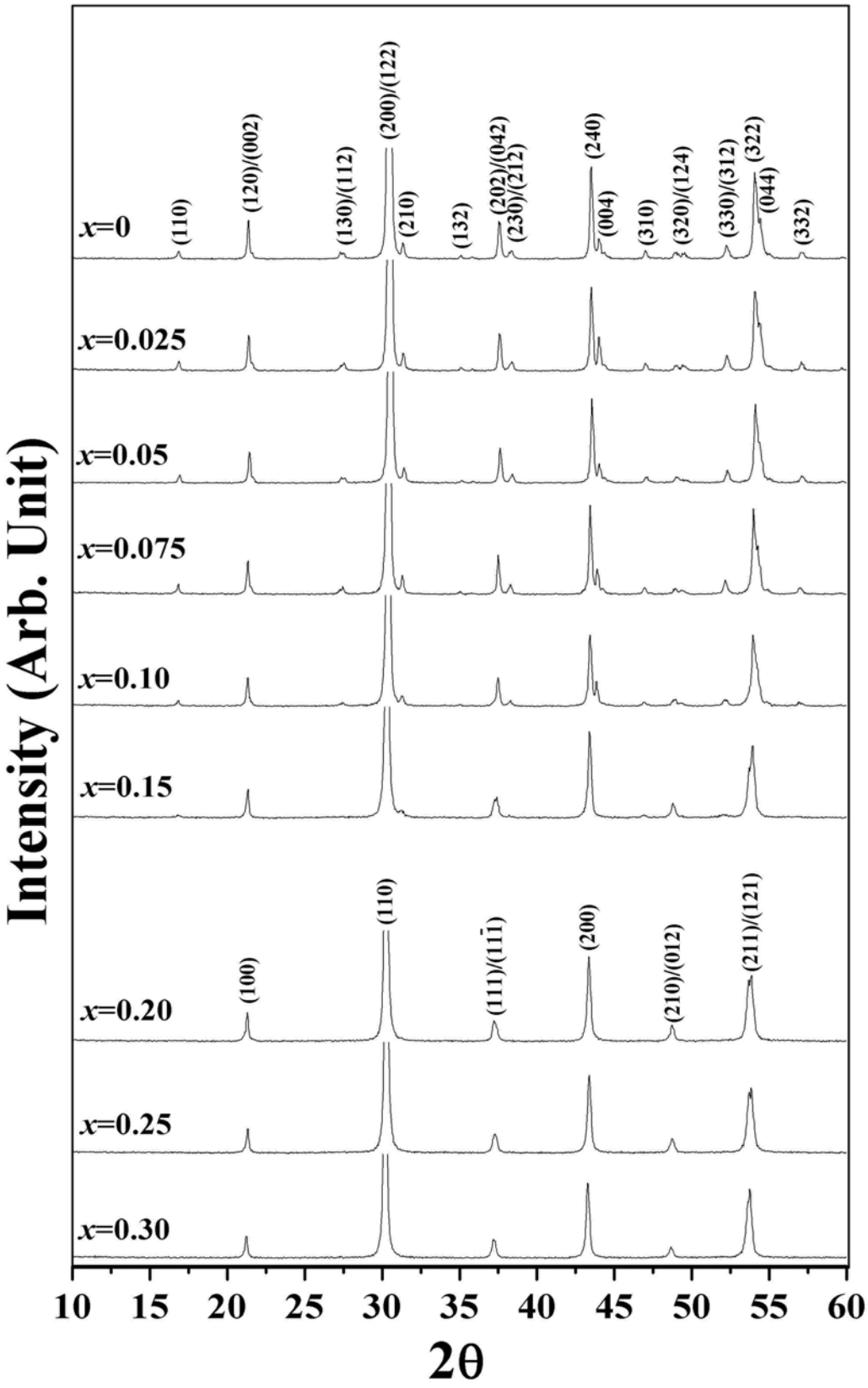


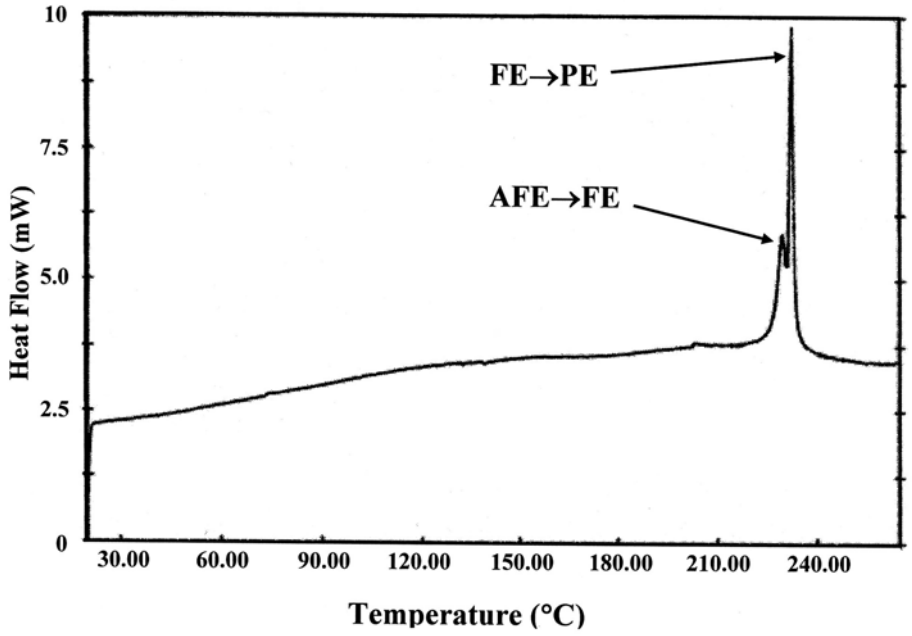
Fig. 1 XRD patterns of sintered pellets of $(Pb_{1-x}Ba_x)ZrO_3$.

rhombohedral and orthorhombic phases coexist for this composition (x = 0.15). For $0.20 \leq x \leq 0.30$, the superlattice lines of the orthorhombic antiferroelectric phase have vanished completely. In addition, the rhombohedral 200 reflection has become a single peak. These indicate that the structure of PBZ is rhombohedral for $0.20 \leq x \leq 0.30$. The results are consistent with work by Pokharel *et al.* who prepared $(Pb_{1-x}Ba_x)ZrO_3$ with semi-wet route method [4,10].

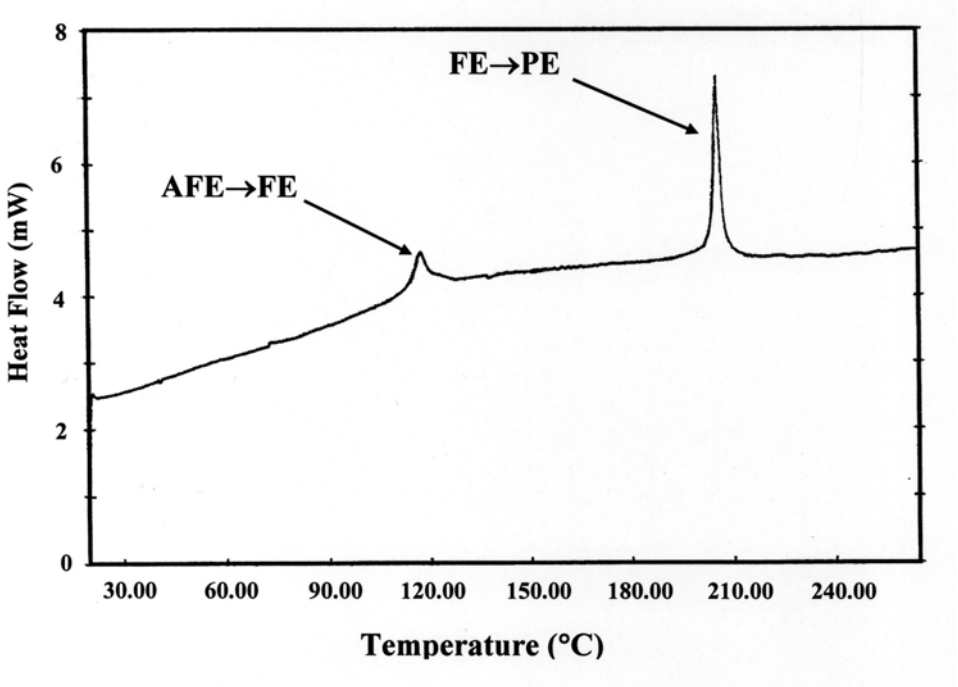
To investigate role of Ba^{2+} content on phase transition of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics, the DSC was performed. A typical result of the DSC of PBZ for composition x=0 and 0.75 is presented in Fig. 2. Table 1 also gives the transition temperature of different composition of PBZ observed from DSC. As shown in Fig. 2(a), two distinct endothermic peaks at about 228.9 and 231.5 ^{o}C were observed for PZ. The lower temperature corresponds to the transition temperature of the AFE $\rightarrow$ FE phase transition, while the higher temperature corresponds to the FE $\rightarrow$ PE phase transition. The AFE $\rightarrow$ FE phase transition was found in the compositions of $0.00 \leq x \leq 0.10$. The peaks shift to lower temperatures with higher the compositions of x, Fig.

Table 1 Phase transitions temperature and enthalpy of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics.

Samples	Phase transitions temperature (^{o}C)		Enthalpy (J/g)	
compositions(x)	AFE $\rightarrow$ FE	FE $\rightarrow$ PE	AFE $\rightarrow$ FE	FE $\rightarrow$ PE
0.000	228.9	231.5	1.73	3.55
0.025	193.3	225.2	1.05	2.31
0.050	154.9	213.3	0.98	2.16
0.075	117.3	205.3	1.05	2.10
0.100	72.5	195.4	0.02	1.68
0.150	-	177.6	-	0.87
0.200	-	157.4	-	0.51
0.250	-	125.0	-	0.28
0.300	-	79.8	-	0.13



(a)



(b)

Fig. 2 DSC thermographs of grounded pellet samples of $(Pb_{1-x}Ba_x)ZrO_3$ for :(a) $x = 0$ and (b) $x = 0.075$.

2(b). The trend of enthalpy for AFE→FE phase transition was found to reduce with progressively increase of Ba^{2+}content as can be seen in Table 1. This result corresponds to the decreasing of AFE phase with increasing amount of Ba^{2+} content.

From Table1, the width of temperature range of FE phase continuously increases progressively with Ba^{2+}content. The width of temperature range of FE phase is around 2.6, 33.9, 58.4, 88.0 and 122.9 ^{o}C for composition x = 0.00, 0.025, 0.050, 0.075 and 0.10, respectively. The enthalpy associated with the FE→PE phase transition gradually reduces with higher Ba^{2+} concentration, Table 1. Gotor *et al.* studied relationships between the structure change of $BaTiO_3$ and its enthalpy by using DSC [13]. They found that the tetragonality (c/a) of $BaTiO_3$ reduces accompanied with the reduction of enthalpy. However, in the present work, the decreasing of ΔH is proportional to the fraction ratio of FE and PE phase in PBZ. From the DSC data of this work, a phase diagram for PBZ prepared by the conventional mixed oxide method is constructed as seen in Fig.3.

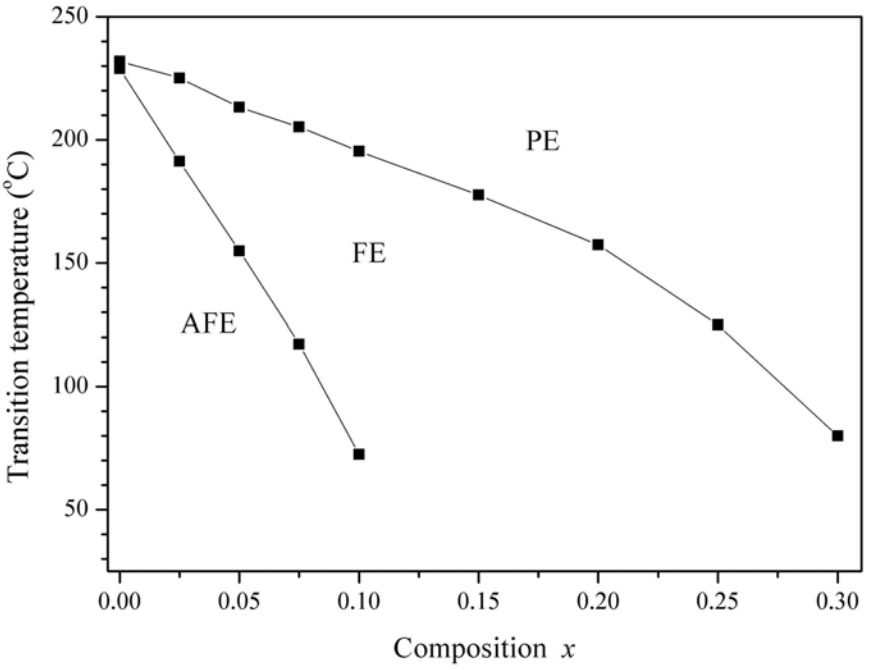


Fig. 3 Phase diagram of PBZ system.

4. Conclusions

The structures of sintered pellets of $(Pb_{1-x}Ba_x)ZrO_3$ for $0 \leq x \leq 0.30$ are orthorhombic and rhombohedral for $0.00 \leq x \leq 0.10$ and $0.20 \leq x \leq 0.30$, respectively. For $x = 0.15$, the two phases coexist at room temperature. The AFE$\rightarrow$FE and FE$\rightarrow$PE phase transition temperatures progressively decrease with continuously increasing Ba^{2+} concentration. The AFE$\rightarrow$FE phase transition is detected for compositions $0.00 \leq x \leq 0.10$. The enthalpy obtained from DSC method, indicated that the proportions of AFE and FE phases in PBZ samples gradually decrease with increasing of Ba^{2+} content. A phase diagram for PBZ ceramics prepared by the conventional mixed oxide method was also present in this work.

References

[1] G. Shirane, Phys. Rev. **86**, 219 (1952).

[2] K.H. Yoon, S.C. Hwang and D. H. Kang, J. Mater. Sci. **32**, 17 (1997).

[3] S-E. Park, M-J. Pan, K. Markowski, S. Yoshikaw and L.E. Cross, J. Appl. Phys. **82**, 1798 (1997).

[4] B. P. Pokharel, M. K. Datta and D. Pandey, J. Mater. Sci. **34**, 691 (1999).

[5] G. Shirane, Phys. Rev. **86**, 219 (1952).

[6] S. Roberts, J. Am. Ceram. Soc. **63**, 33 (1950).

[7] Z. Ujma, J. Handerek, M. Pawelczyk and D. Dmytrow, Ferroelectrics **129**,127 (1992).

[8] B. P. Pokharel and D. Pandey, J. Appl. Phys. **86**, 3327 (1999).

[9] B. P. Pokharel and D. Pandey, J. Appl. Phys. **90**, 2985 (2001).

[10] B. P. Pokharel and D. Pandey, J. Appl. Phys. **88**, 5364 (2000).

[11] T. Bongkarn, G. Rujijanagul and S. J. Milne, Mater. Lett. **59**, 1200 (2005).

[12] Z. Ujma, J. Handerak and M. Kupiszewska, J. Eur. Ceram. Soc. **22**, 817 (2002).

[13] F.J. Gotor, C. Real, M.J. Dianez and J.M. Criado, J. Solid State Chem. **123**, 301 (1996).

Effect of excess PbO on phase formation, microstructure and dielectric properties of $(Pb_{0.975}Ba_{0.025})ZrO_3$ ceramics

Abstract

Polycrystalline samples of $(Pb_{0.975}Ba_{0.025})ZrO_3$ (PBZ2.5) were prepared by a mixed oxide, solid-state reaction method. Excess PbO (1,3, 5 or 10 wt %) was introduced prior to powder calcination to compensate for any PbO that may have been lost from the samples due to volatilsation during heat treatments. The phase structure was analyzed by XRD. Pure PBZ2.5 phase was observed in all of the ceramic samples. Microstructurally, excess PbO produced an increase in average grain size, from ~ 0.5 μm for no excess to ~0.8 μm for excess PbO. Dielectric constant-temperature plots showed a maximum peak value of 8070, for the 1 wt % sample which was also the densest sample.

1. INTRODUCTION

The effect of Ba^{2+} ion substitution on physical properties and phase transitions behavior of $(Pb_{1-x}Ba_x)ZrO_3$ (PBZ) has been investigated by many authors (Roberts, 1953; Shirane, 1952; Pokharel *et al*., 1999). The first one was Roberts but he did not get any evidence for the antiferroelectric (AFE) to ferroelectric (FE) phase transition (Roberts, 1953). Later, Shirane investigated the phase transformation behavior of $(Pb_{1-x}Ba_x)ZrO_3$ for $0 \leq x \leq 0.30$ and reported that the ferroelectric intermediate phase does not appear until the Ba^{2+} concentration exceeds the threshold value at about 5 mol% (Shirane, 1952). The temperature range of this intermediate phase increases with the Ba^{2+} concentration. On the contrary, Ujma *et al.* reported the FE phase

existence in PBZ containing up to 5 mol% Ba^{2+}, with dielectric properties different from the previous papers (Ujma *et al.*, 1992). Recently, Pokharel *et al.* found unusually wide thermal hysteresis in the AFE-FE phase transition measured by dielectric measurement during heating and cooling cycles (e.g., nearly 100 ^{o}C for x = 0.05 in contrast to about 11 ^{o}C for pure PZ) and an irreversibility of the AFE to FE transformation temperature during the cooling cycle for x = 0.10 (Pokharel and Pandey, 1999). Different research groups reported the different results of AFE-FE phase transition (Yoon *et al*., 1997; Pokharel and Pandey, 2001; Pokharel and Pandey, 1999; Ujma *et al*., 1992; Pokharel and Pandey, 2000). Pokharel *et al.* proposed that the processing method used to prepare the PBZ powders may be important in influencing phase formation. Moreover, another factor to consider is also the possible effect of PbO loss due to evaporation during high temperature processing. The PbO vapour-pressure may be sufficient to create compositional changes in the powders. Moreover, any variation in Pb and O ion vacancy concentrations may be important in terms of phase stability.

Hence, the present work studied the effect of PbO contained on the phase formation and properties of PBZ2.5 which prepared via solid state reaction method. Structural phase formations, microstructure and densification of PBZ2.5 ceramics are investigated. Dielectric measurements are used for studies the details of AFE-FE and FE-paraelectric (PE) phase transitions

2. EXPERIMENTAL PROCEDURE

The $(Pb_{0.975}Ba_{0.025})ZrO_3$ (PBZ2.5) ceramics were prepared by using a conventional mixed oxide method. The raw materials of PbO (purity 99.9 %, supplied by Johnson Matthey GmbH, UK), ZrO_2 (purity 99 %, supplied by Aldrich, UK) and $BaCO_3$

(purity 99.9 %, supplied by Johnson Matthey GmbH, UK) were weighed and mixed. Each mixture of the starting powders was milled and mixed in a ball mill, as well as wet-homogenized with acetone for 24 h using zirconia grinding media. The suspensions were dried and the powders were ground using an agate mortar and sieved (300 μm) in to fine powder. All obtained powders were calcined at 1000 °C for 1 h. An excess of PbO, equivalent to 0, 1, 3, 5 or 10 wt%, was applied prior to ball milling before calcination. The calcined powders were reground by wet ball-milling with 1wt% binder (B-5 supplied by Rohn-Haas, Germany) for 24 h. The calcined powders with binder were dried, crushed and sieved again. The powder mixtures were isostatically pressed at 80 MPa into a pellet of 15 mm in diameter.

Finally, the pellets were fired in an alumina crucible and sintered at 1200 °C for 4 h. In order to minimize the loss of lead due to vaporization, the PbO atmosphere for the sintering was maintained using $PbZrO_3$ as the spacer powder. The phase evolution of the calcined powder and sintered pellets was determined using a diffractometer (Philips ADP1700). The density of the sintered samples was measured by Archimedes' method with distilled water as the fluid medium. The microstructure developments of the sintered samples were examined using scanning electron microscopy (JEOL, JSM5910). The sintered samples were prepared for electrical property measurements by first polishing and then gold sputtering on to the clean pellet faces. The dielectric measurements were carried out at 1 kHz using a HIOKI 3532-50 impedance analyzer, from room temperature to 300 °C with a heating rate of 0.5 °C/min was controlled by a computer.

3. RESULTS AND DISCUSSTION

Figure 1 show XRD patterns of calcined powders made from starting mixtures containing different levels of PbO. For the sample made with no excess PbO, only

the PBZ phase was observed (Pokharel *et al*., 1999). On the other hand, small amounts of PbO (JCPDS no. 76-1796, 2000; JCPDS no. 85-1287, 2000) was clearly present in the 10 wt% excess PbO sample, and there was also some evidence of these phases being present, in the 5 wt% , and to a much lesser extent, in the 3 wt% samples. The presence of 'free' PbO is expected in the higher excess samples. The XRD data for sintered samples revealed that no PbO was present in any sample, indicating that the excess PbO beyond that required to maintain compositional control (assumed) in the PBZ2.5 powder was eliminated from the sample by volatilization during sintering at 1200 ºC (Figure 2).

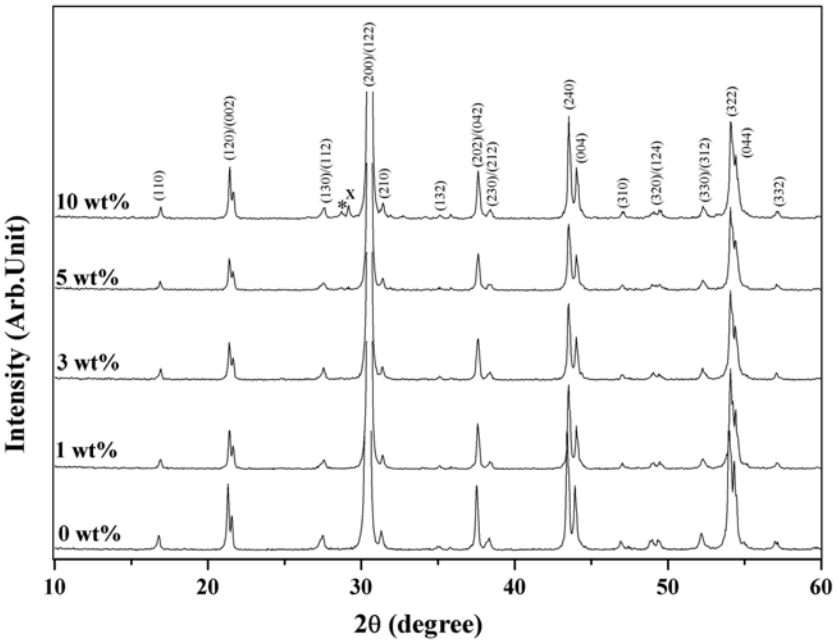


Figure 1 XRD patterns of calcined powders of PBZ2.5 made from starting powders containing different amounts of excess PbO: (x) PbO (orthorhombic phase) and (*) PbO (tetragonal phase).

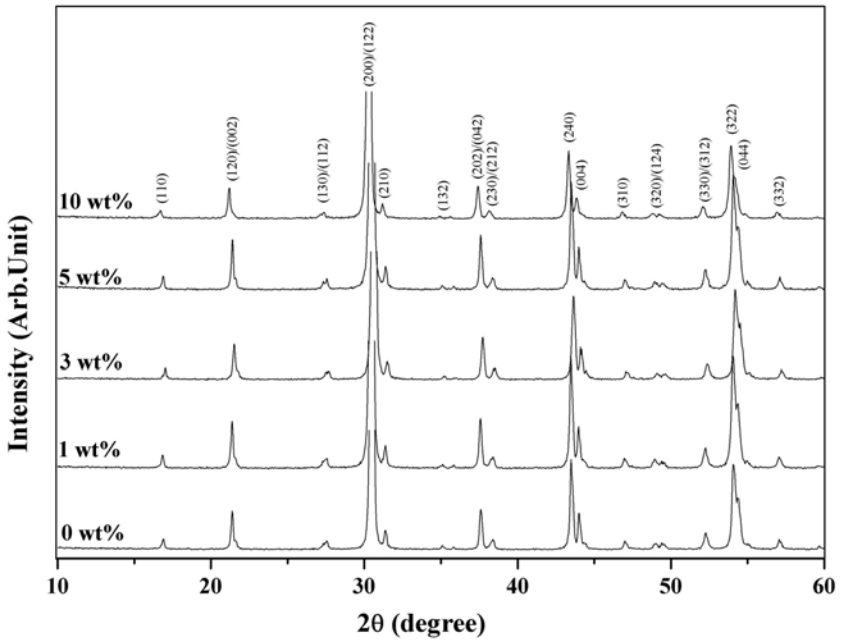


Figure 2 XRD patterns of sintered pellets of PBZ2.5 made from starting powders containing different amounts of excess PbO.

The density of PBZ2.5 ceramics as a function of amount of PbO content is shown in Table 1. The maximum density was 7.90 g/cm^3 for the sample containing PbO 1 wt%. At the higher PbO contained, the density decreased with increasing the excess PbO. The results could be caused of loss of PbO from the compact pellet which increases its porosity. The presence of PbO rich liquid phase usually helps higher densification in sintering. However, the large amount of PbO liquid phase can produce an initial rapid densification but a low final density as a result of void formation due to the PbO evaporation. As a consequence the porosity of the pellet increase and this is not removed by solid state sintering (Kingon and Clark, 1983).

Figure 3 shows SEM micrographs of the surface for the PBZ2.5 ceramics at various PbO contents. By using the linear intercept method, the average grain sizes were 0.5,

0.7, 0.8, 0.7 and 0.7 μm for samples with the excess PbO of 0, 1, 3, 5 and 10 wt%, respectively. The grain size of the excess PbO was larger than the base composition. Moreover, the grain size distribution at the lower PbO content is more uniform than that of the samples contained at the higher PbO. Similar results were found in many lead base ceramics (Garg and Agrawal, 1999; Zhou *et al*., 2004).

Table 1 Density, values of peak dielectric constant and transitions temperature.

Amount of PbO Excess (wt.%)	Density (g/cm^3)	Maximum dielectric constant at the FE:PE phase transition	Transition temperature (^oC)	
			AFE:FE	FE:PE
0	7.88	7485	184.1	223.6
1	7.90	8070	189.8	223.6
3	7.89	7960	189.9	223.5
5	7.81	7025	190.8	224.4
10	7.77	6420	189.6	224.1

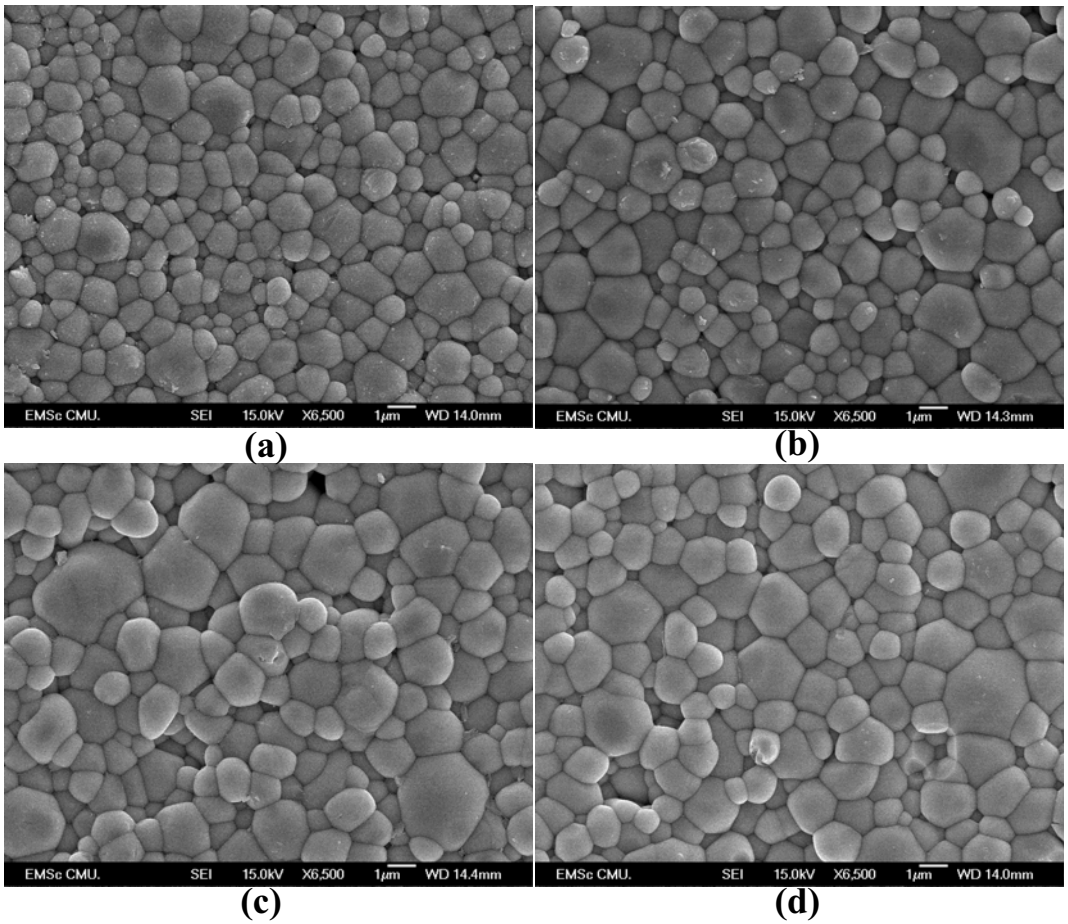


Figure 3 SEM micrographs of as-sintered of sintered PBZ2.5 pellets made from starting powders with different PbO contents: (a) 0 wt%, (b) 1 wt%, (c) 3 wt% and (d) 10 wt%.

The dielectric constant of various excess PbO as a function temperature is shown in Figure 4. The FE-PE phase transition occurred at ~ 223-224 ºC for all samples, Table 1. There was however an increase in peak dielectric constant from 7485 for the 0% sample to 8070 for the 1 wt% sample, followed by reductions for the 3, 5 and 10 wt% samples, Table 1. This trend matches that of the sintered densities, i.e. the lower density samples gave lower measured dielectric constants. There have been observation reported that compositions with excess PbO additions greater than 2.8 mol% results in degraded electrical properties (Swartz *et al*., 2004). Furthermore, the amounts of excess PbO were found to have a significant effect on the AFE-FE

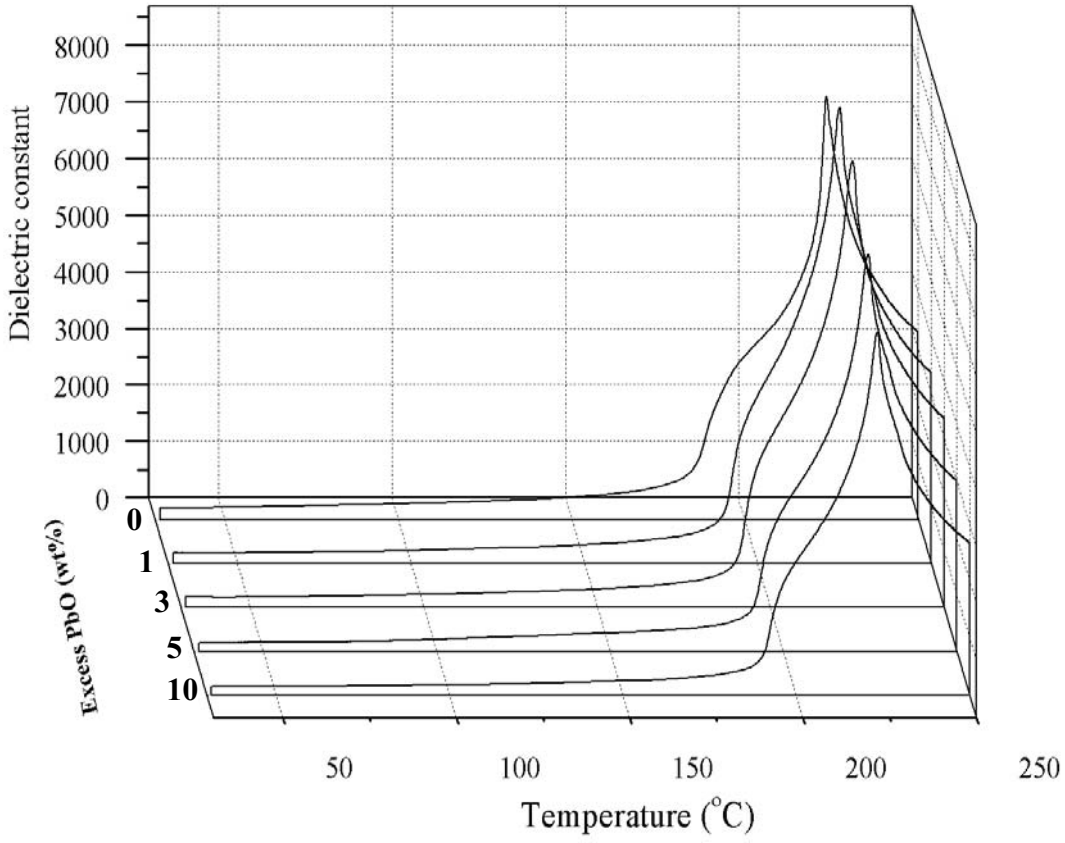


Figure 4 Dielectric constant versus temperature for PBZ2.5 ceramics made from powders with different amounts of starting excess PbO.

4. CONCLUSION

The $(Pb_{0.975}Ba_{0.025})ZrO_3$ ceramics were fabricated with various excess PbO contents. The effect of lead excess on the properties of the ceramics was studied. The pure perovskite orthorhombic phase was observed for all size in the sintered samples, from an average of ~0.5 μm for the unmodified composition to ~0.8 μm for the excess PbO compositions. The results indicate that ~ 1 wt% excess PbO produced the highest density ceramics, exhibiting the maximum value of the dielectric constant.

REFERENCE

Garg, A.and Agrawal, D.C.1999. Effect of Net PbO Content on Mechanical and Electromechanical Properties of Lead Zirconate Titanate Ceramics. *Mat Sci Eng B-Solid.* 56: 46.

Hagimura, A.and Uchino, K. 1989. Impurity Doping Effect on Electrostrictive Properties of $(Pb,Ba)(Zr,Ti)O_3$. *Ferroelectrics.* 93: 373.

Kingon, A.I. and Clark, J.B. 1983.Sintering of PZT Ceramics: I, Atmosphere Control. *J. Am. Ceram. Soc*. 66: 253.

Kingon, A.I. and Clark, J.B. 1983. Sintering of PZT Ceramics: II, Effect of PbO Content on Densification Kinetics. *J. Am. Ceram. Soc*. 66: 256.

Pokharel, B. P., Datta, M. K. and Pandey, D. 1999. Influence of Calcination and Sintering Temperatures on the Structure of $(Pb_{1-x}Ba_x)ZrO_3$. *J. Mater. Sci.* 34: 691.

Pokharel, B. P. and Pandey, D. 1999. Irreversibility of the Antiferroelectric to Ferroelectric Phase Transition $(Pb_{0.90}Ba_{0.10})ZrO_3$ Ceramics. *J. Appl. Phys.* 86: 3327.

Pokharel, B. P. and Pandey, D. 2000. Dielectric Studies of Phase Transitions in $(Pb_{1-x}Ba_x)ZrO_3$. *J. Appl. Phys.* 88: 5364.

Pokharel, B. P. and Pandey, D. 2001. High Temperature X-ray Diffractometer Studies on Antiferroelelectric and Ferroelectric Phase Transitions in $(Pb_{1-x}Ba_x)ZrO_3$ (x=0.05, 0.10). *J. Appl. Phys.* 90: 2985.

Pokharel, B. P., Ranjan, R.and Pandey, D. 1999. Rhombohedral Superlattice Structure and Relaxor Ferroelectric Behavior of $(Pb_{0.70}Ba_{0.30})ZrO_3$ Ceamics. *Appl. Phys. Lett.* 74: 756.

Powder Diffraction File no.76-1796, International Centre for Diffraction Data, Newton Square, PA, 2000.

Powder Diffraction File no.85-1287, International Centre for Diffraction Data, Newton Square, PA, 2000.

Roberts, S. 1953. Dielectric Properties of Lead Zirconate and Barium-Lead Zirconate. *J. Am. Ceram. Soc*. 33: 63.

Swartz, S.L., Shrout, T.R., Schulze, W.A. and Cross, L.E. 1984. Dielectric Properties of Lead-Magnesium Niobate Ceramics. *J. Am. Ceram. Soc.* 67: 311.

Shirane, G. 1952. Ferroelectricity and Antiferroelectricity in Ceramics $PbZrO_3$ Containing Ba or Sr. *Phys. Rev.* 86: 219.

Shirane, G. and Hoshino, S. 1953. X-ray Study of Phase Transitions in $PbZrO_3$ Containing Ba or Sr. *Acta Cryst.* 5: 530.

Ujma, Z., Handerek, J., Pawelczyk, M. and Dmytrow, D.1992. Phase Composition and Dielectric Properties of Lead Barium Zirconate Solid Solutions. *Ferroelectrics.* 129: 127.

Yoon, K. H., Hwang, S. C., and Kang, D. H. 1997. Dielectric and Field-induced Strain Behavior of $(Pb_{1-x}Ba_x)ZrO_3$ Ceramics. *J. Mater. Sci*. 32: 17.

Zhou, L., Zimmermann, A., Zeng, Y. and Aldinger, F. J. 2004. Bipolar Electric Fatigue Behavior as a Function of Field Strength in Antiferroelectric $(Pb,Ba,La)(Zr,Sn,Ti)O_3$. *Mater. Sci.: Mat. Elec.* 15: 145.

Effect of Excess Lead Oxide on Phase Transitions and Physical Properties of Perovskite Lead Barium Zirconate Ceramics

Abstract

Effect of excess PbO on phase transitions and physical properties of perovskite $(Pb_{0.90}Ba_{0.10})ZrO_3$ ceramics have been investigated. The $(Pb_{0.90}Ba_{0.10})ZrO_3$ ceramics were prepared via the conventional mixed oxide method. Excess PbO (1, 3, 5, and 10 wt%) was introduced prior to powder calcination. The phase formation and phase transition of $(Pb_{0.90}Ba_{0.10})ZrO_3$ ceramics were characterized by X-ray diffraction and thermal analysis. The result indicated that excess PbO showed an effect on antiferroelectric to ferroelectric phase transition. However, it was not found significant effect of excess PbO on ferroelectric to paraelectric transition temperature.

1. INTRODUCTION

$(Pb_{1-x}Ba_x)ZrO_3$ (PBZ) was discovered by Roberts in 1950 [1]. Later on, many authors have investigated the properties of PBZ, especially its phase transitions [1-7]. Shirane [3] was one of who first demonstrated the antiferroelectric to ferroelectric (AFE $\rightarrow$ FE) phase transition in PBZ solid solution compositions with $x \geq 0.05$. In PBZ, the AFE and FE phases were characterized as orthorhombic and rhombohedral structure, repectively. It is reported that the AFE $\rightarrow$ FE phase transition produces a large increase in volume [5]. Furthermore, the electric-field required to induce AFE $\rightarrow$ FE switching is much lower than for $PbZrO_3$ (PZ) which has created interest in PBZ for potential use in large displacement actuator devices requiring low switching voltages [8].

Different research groups reported the different results of AFE $\rightarrow$ FE phase transition [1,4-8]. Several authors [4,6] have found no evidence of any AFE $\rightarrow$ FE transitions, whilst there have been a few reports showing an AFE$\rightarrow$FE transition

without corresponding FE→AFE transition on cooling [2]. It is suggested that the processing method used to prepare the PBZ powders may be important in influencing phase formation and phase transitions [7]. An important factor to consider is the possible effect of PbO loss due to evaporation during high temperature processing [7]. Hence, the present work studied the effect of PbO content on the phase transition and properties of $(Pb_{0.90}Ba_{0.10})ZrO_3$ (PBZ10).

2. EXPERIMENTAL

The raw materials of PbO, ZrO_2, and $BaCO_3$ were weighed and mixed. Each mixture of the starting powders was milled using zirconia grinding media. After drying and sieving, the mixture was calcined at 850 °C for 6 h. An excess of PbO, equivalent to 0, 1, 3, 5, and 10wt%, was applied prior to ball milling before calcination. The calcined powders were reground by wet ball-milling with 1wt% binder for 24 h. The calcined powders with binder were dried, crushed and sieved again. The powder mixtures were isostatically pressed into pellets then the pellets were sintered at 1325 °C for 4 h in an alumina crucible. In order to minimize the loss of lead due to vaporization, PZ was used as the spacer powder. Thermogravimetry (TG) and differential thermal analysis (DTA) techniques were used to monitor the reactions between the oxide precursors. The thermal expansion of the ceramics samples was measured using a dilatometer. The phase transition temperatures were determined by a differential scanning calorimeter (DSC). All techniques in thermal analysis were performed at a heating of 10°C/min.

3. RESULTS AND DISCUSSION

The TG and DTA curves recorded for an equimolar mixture of lead oxide, barium carbonate and zirconium oxide (PbO: $BaCO_3$: ZrO_2 = 1:1:1), are given in Fig. 1. The TG curve shows three interesting weight losses below 800 ^oC. The first weight

loss occurs below 150 ^{o}C, attribute to the vaporization of water. The second one between 270 to 350 ^{o}C, relate to the elimination of organic residual from the milling process. The last one above 700 ^{o}C, relate to the solid-state reaction between the starting materials. From these data, the temperature of 850 ^{o}C was selected for calcination to ensure the complete solid-state reaction.

Fig. 2 shows XRD patterns of sintered samples. Pure perovskite of PBZ phase was observed for the whole range of the compositions. The intensity ratio of 004/240 peaks ($I_{004/240}$) may be taken as a qualitative indicator of the relative proportion of the orthorhombic (AFE) and rhombohedral (FE) phases. For a purely orthorhombic pattern, $I_{004/240} \approx 0.5$ and this value decreases with

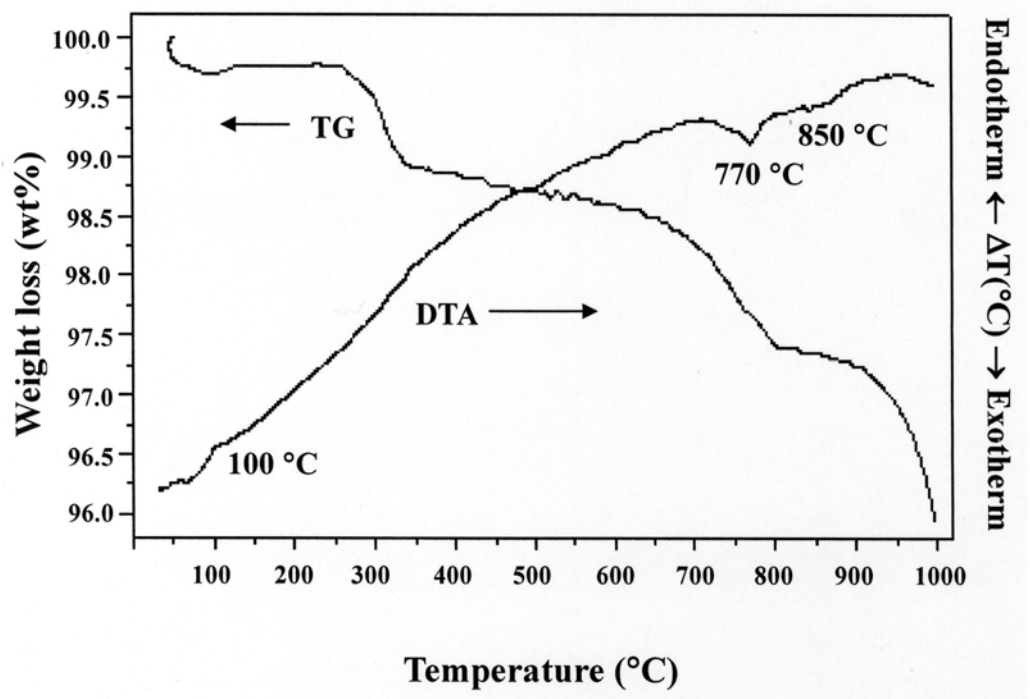


Fig. 1 TG and DTA curves for the mixture of PbO, $BaCO_3$ and ZrO_2 powders.

increasing amounts of coexisting rhombohedral phase [8]. In the present work, $I_{004/240}$ increase with increasing excess PbO content up to 1 wt%. For the higher PbO content, the intensity ratio continually decrease, Table 1. The result indicates less

rhombohedral and more orthorhombic phase in the 1 wt% excess PbO sample. The lattice parameter and unit cell volume of PBZ10 obtained by least square refinement method is shown in Table 1. The unit cell volume slightly increases with increasing excess PbO content up to 1 wt%. For the higher PbO content, the unit cell volumes continually decrease.

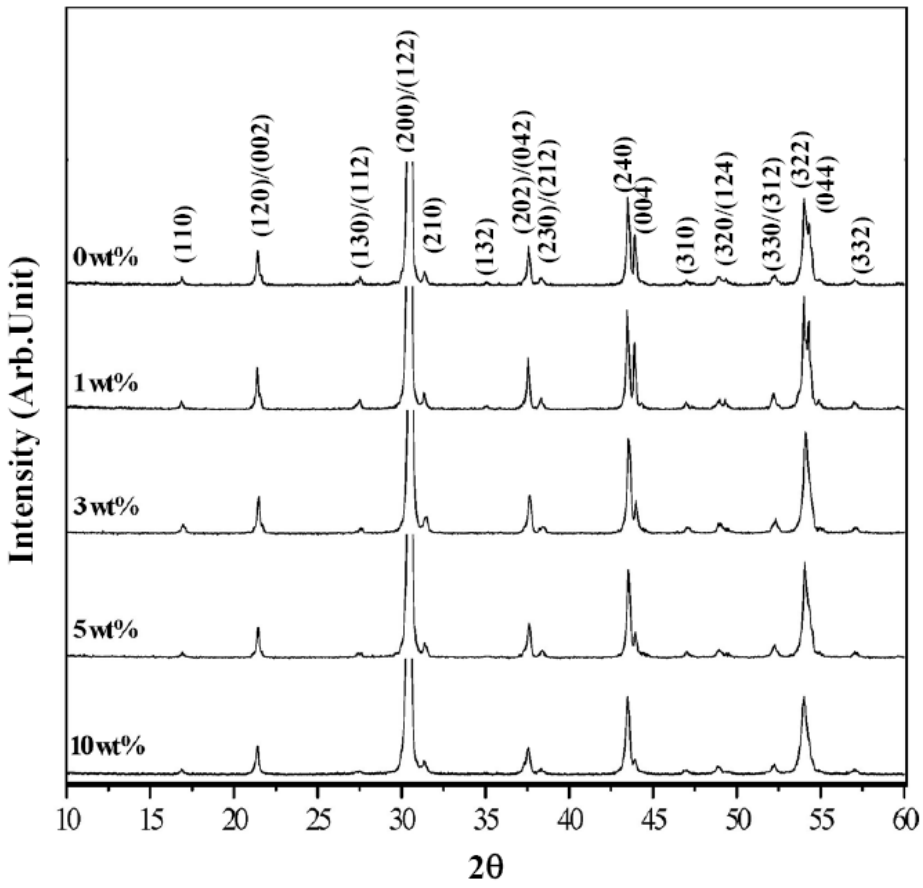


Fig. 2 XRD patterns of PBZ10 ceramics made from starting powders with different amounts of starting excess PbO.

The measurements of the length of a specimen at various temperatures of solid materials are usually applied for the determination of the kinetics of phase transformation of PZ [12, 13]. The dilatometric thermal expansion of PBZ10 with

excess PbO on heating cycle is plotted in Fig. 3. The discontinuously curves can be attributed to the FE to PE phase transition with rising temperature [3,12]. However, the anomaly of AFE→FE phase transition could not be observed due to sensitivity limit of the dilatometer.

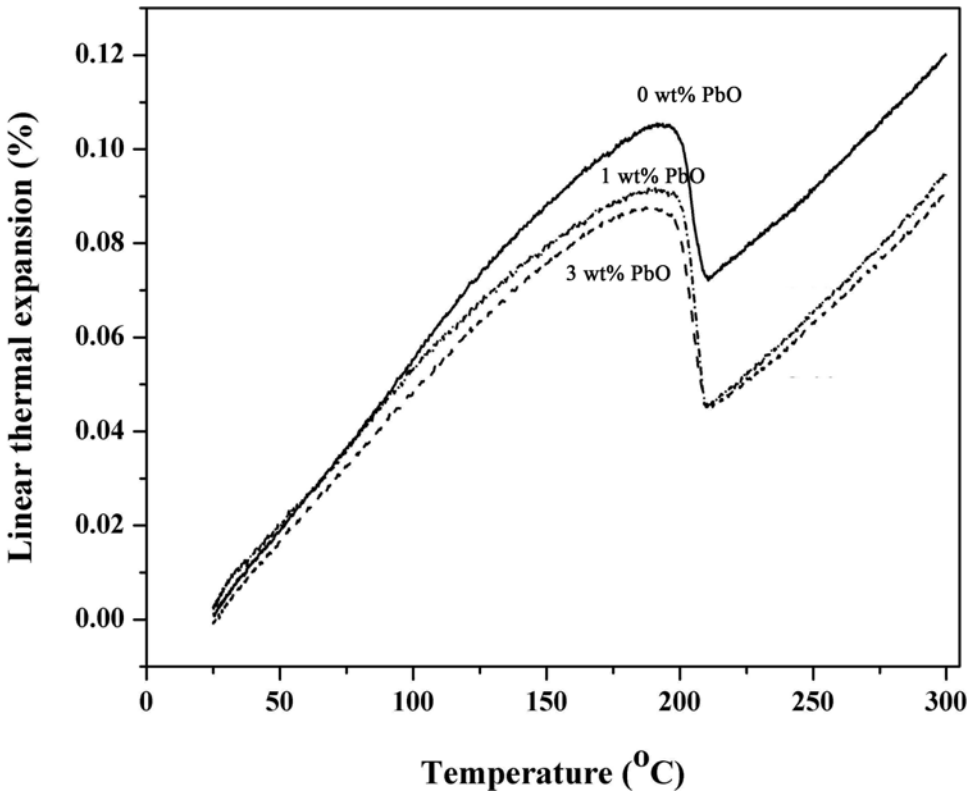


Fig. 3 Linear thermal expansion versus temperature of PBZ10 ceramics made from starting powders with different amounts of starting excess PbO.

DSC results of PBZ10 with excess PbO on heating cycle are given in Fig. 4. The two distinct endothermic peaks were found. The lower temperature peak is obviously smaller than the higher temperature one. These peaks can be associated with the AFE →FE and FE →PE phase transition, respectively. The listed of AFE→FE and FE→PE phase transition temperature are presented in Table 1.

Table 1 Intensity ratio of 004/240 peak, lattice parameter, unit cell volume, density and transition temperature of PBZ10 ceramics with different amounts of excess PbO.

Amount of excess PbO (wt%)	$I_{004/240}$	Lattice parameter (Å)			Unit cell volume ($Å^3$)	Transition Temperature (^oC)			
		a	b	c		Dilatometer		DSC	
						AFE → FE	FE → PE	AFE → FE	FE → PE
0	0.57	5.8924	11.6848	8.2158	565.6703	-	197.2	72.81	195.28
1	0.67	5.8966	11.6906	8.2159	566.3614	-	196.7	76.36	196.78
3	0.32	5.8936	11.6942	8.2153	566.2062	-	196.0	73.16	196.63
5	0.29	5.8884	11.6737	8.2119	564.4812	-	193.9	72.33	194.31
10	0.20	5.8881	11.6707	8.2068	563.9569	-	194.4	72.50	195.54

There is no direction trend for FE → PE transition temperature. However, the FE → PE transition temperature was found between 194 -197 ºC. The AFE → FE transition temperature increases with increasing amount of PbO up to 1wt% then it decreases with further amount of PbO. This result corresponds to the XRD result, indicating the AFE → FE transition is sensitive to the Pb ions in the compositions. Scott and Burns reported that the temperature interval of the ferroelectric phase (ΔFE) in $PbZrO_3$ depends on stoichiometry [14]. They found that the minimum of ΔFE occurs for samples containing stoichiometric composition. In this study, the resulting change in defect chemistry may be the reson to the change in the transition temperature.

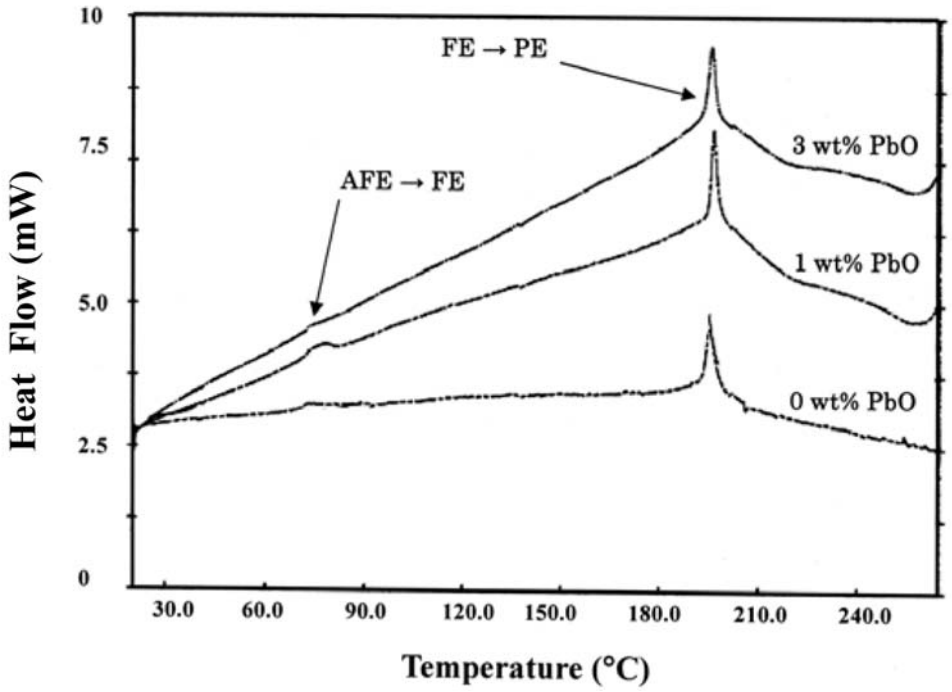


Fig. 4 DSC thermographs of PBZ10 ceramics made from starting powders with different amounts of starting excess PbO.

4. CONCLUSIONS

The PBZ10 ceramics with different of excess PbO levels were prepared by conventional mixed oxide method. The sample contained 1wt% excess PbO exhibited the maximum of AFE→FE transition temperature. However, there is no significant effect of excess PbO content on FE→PE transition temperature. The results indicate that the AFE→FE transition is sensitive to the Pb ions in the compositions.

REFERENCES

[1] S. Roberts, J. Am. Ceram. Soc. **63**, 33 (1950).

[2] B. P. Pokharel, M. K. Datta and D. Pandey, J. Mater. Sci. **34**, 691 (1999).

[3] G. Shirane, Phys. Rev. **86**, 219 (1952).

[4] K. H. Yoon, S. C. Hwang and D. H. Kang, J. Mater. Sci. **32**, 17 (1997).

[5] B. P. Pokharel and D. Pandey, J. Appl. Phys. **90**, 2985 (2001).

[6] Z. Ujma, J. Handerek, M. Pawelczyk and D. Dmytrow, Ferroelectrics **129**, 127 (1992).

[7] B. P. Pokharel and D. Pandey, J. Appl. Phys. **88**, 5364 (2000).

[8] B. P. Pokharel and D. Pandey, J. Appl. Phys. **86**, 3327 (1999).

[9] Powder Diffraction File no.81-2042, International Centre for Diffraction Data, Newton Square, PA (2000).

[10] Powder Diffraction File no.76-1796, International Centre for Diffraction Data, Newton Square, PA (2000).

[11] Powder Diffraction File no.85-1287, International Centre for Diffraction Data, Newton Square, PA (2000).

[12] V. J. Tennery, J. Am. Ceram. Soc. **49**, 483. (1966).

[13] L. Goulpeau, Sov. Phys. Solid St. **8**, 1970 (1967).

[14] B. A. Scott and G. Burns, J. Am. Ceram. Soc. **55**, 331 (1972).

Antiferroelectric-ferroelectric phase transitions in $Pb_{1-x}Ba_xZrO_3$ ceramics: effect of PbO

Abstract

The irreversibility of the antiferroelectric (AFE) to ferroelectric (FE) phase transition in $Pb_{1-x}Ba_xZrO_3$, x = 0.75-0.1 compositions is shown to be a consequence of lattice vacancies arising from PbO evaporation during ceramic processing. Previously the absence of a FE→AFE cooling transition was thought to be due to transformational strain and the fragmentation of ferroelectric domains. Appropriate compensating levels of excess PbO added to starting powders generate the FE→AFE transition. For lower levels of Ba^{2+} substitution, x = 0.05, the transition is reversible in non-compensated samples, but PbO compensation raises the FE→AFE transition temperature by ~25 °C.

3. INTRODUCTION

Lead zirconate, $PbZrO_3$, transforms on heating, from an orthorhombic antiferroelectric (AFE) to a rhombohedral ferroelectric (FE) phase just below the Curie temperature of 233 °C.[1-5] The antiferroelectric-ferroelectric phase transition can be induced by application of an electric field, or by hydrostatic pressure.[6,7] Substitution of Ba^{2+} for Pb^{2+} ions lowers transition temperatures, reduces the switching field and increases the volume change associated with the field-induced transition.[8] Consequently the $Pb_{1-x}Ba_xZrO_3$ system (PBZ) is of interest for energy storage and actuator applications. [8-9] In addition, for compositions which are ferroelectric at room-temperature, favourable fatigue resistance has been demonstrated in thin-films, whilst relaxor behaviour has also been investigated.[10, 11]

For antiferroelectric $Pb_{0.9}Ba_{0.1}ZrO_3$, no heating transition to the ferroelectric phase is reported to occur in ceramics made by conventional mixed-oxide processing involving powder calcination at ~ 1000 °C.[8-9] However for ceramics made from chemically co-precipitated $Pb_{0.9}Ba_{0.1}CO_3$ powders, in which $Pb_{0.9}Ba_{0.1}ZrO_3$ calcination temperatures could be reduced to ~ 850 °C, an AFE→FE heating transition was realised, but the transition was irreversible on the cooling cycle. The latter samples were assumed not to exhibit any PbO loss due to volatilisation during ceramic processing and to be chemically homogeneous.[9] The realisation of a heating AFE→FE transition, at ~114 °C, was thought to be due to a more homogeneous Pb^{2+}/Ba^{2+} ion distribution compared to mixed-oxide samples. The absence of the cooling FE→AFE transition was proposed to be a result of a large transformational strain associated with an ~ 0.8 % increase in unit-cell volume at the AFE→FE heating transition. This was considered to cause fine-scale fragmentation of ferroelectric domains which altered the free-energy balance in favour of retention of the FE phase.[8,9] No AFE→ FE transition was recorded on cooling to -50 °C. Partial recovery of the AFE phase was evident after prolonged ageing at room-temperature for ten months.[8] This was thought to be due to the 'healing' of fragmented domains and eradication of broken and dangling bonds over time.[8] Here it is demonstrated that for mixed-oxide samples the AFE→FE transition in $Pb_{0.9}Ba_{0.1}ZrO_3$, and more notably the reverse FE→AFE cooling transition can be realised during normal heating–cooling cycles through additions of excess PbO to offset volatilisation losses. Lattice vacancies are known to affect ferroelectric transitions in other perovskites [16] and for $PbZrO_3$ it has been shown that Pb^{2+} and O^{2-} vacancies induced by annealing under reduced pressure extend the temperature range over which the FE phase exists.[17, 18]

4. EXPERIMENTAL PROCEDURE

Excess PbO (1, 3, 5,10 wt %) was introduced into the precursor mixture of PbO, $BaCO_3$ and ZrO_2, followed by conventional ball-milling, and calcination at 1000 °C for 1 h in covered alumina crucibles. Pellets were pressed at 100 MPa and sintered at 1200 °C for 3 h, whilst embedded in a $PbZrO_3$ powder in a closed crucible. Phase transitions were investigated for $Pb_{1-x}Ba_xZrO_3$, x = 0.05, 0.075 and 0.1 ceramics using differntial scanning calorimetry (PerkinElmer DSC7, heating/cooling rate 10 °C/min). Onset DSC transition temperatures, T_{AFE-FE} and T_{FE-AFE}, are quoted, unless otherwise stated; transition enthalpy was calculated using instrument software. Relative permittivity, ε_r, measurements were carried out from room temperature to 250 °C using an impedance analyser (HIOKI 3532-50, heating/cooling rate 1 °C/min).

3. RESULTS AND DISCUSSION

Plots of ε_r versus temperature for an x= 0.1 mixed-oxide ceramic, made without excess PbO in the starting mixture, were in agreement with literature reports, in that no AFE→FE heating transition was detected. However, using DSC, a faint peak, centered at ~ 70 °C, appeared on the heating cycle suggesting a limited volume of the sample, possibly close to the surface, had transformed to the higher volume FE phase.

The DSC technique was used as the primary tool to investigate the effects of excess PbO on phase transitions. Transition temperatures, including paralectric (PE) transitions, are summarised in Table I. There were no significant changes in T_{AFE-FE} or T_{FE-PE} with added PbO. Introducing 5 wt% or 10 wt % PbO to the x = 0.1 precursor powder increased the size of the AFE→FE heating peak at ~ 70 °C and generated a cooling DSC anomaly at 4 °C for 5 wt %, and at - 3 °C for 10 wt % PbO, Fig 1. A second DSC run, a few minutes after the first cycle, displayed a AFE→FE heating

peak at a similar temperature, and with a similar transition enthalpy to the first run, confirming that the cooling peak represented a FE→AFE transition. This is the first report of a normal, reversible AFE↔FE transition in any type of $Pb_{0.9}Ba_{0.1}ZrO_3$ ceramic.

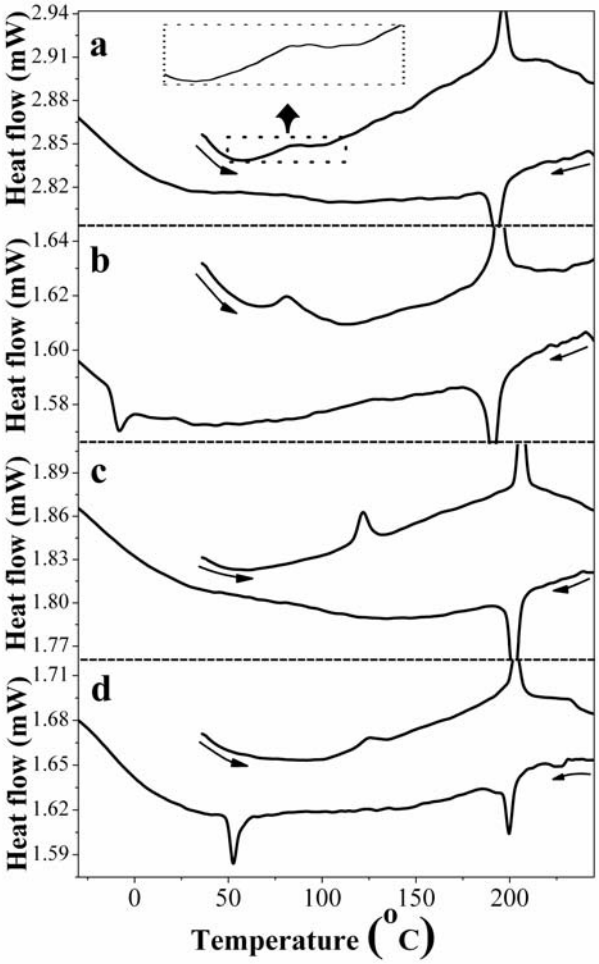


Fig 1 DSC plots showing heating and cooling cycles for $Pb_{1-x}Ba_xZrO_3$: (a) x = 0.1, (b) x = 0.1 + 10 wt % PbO, (c) x = 0.075 and (d) x = 0.075 +5 wt % PbO.

The AFE→FE transition temperature of $Pb_{0.9}Ba_{0.1}ZrO_3$ ceramics made from chemically-precipitated powders quoted in the literature, ~ 114 °C, is considerably higher than found here (onset and peak values 71 °C and 83°C respectively, Table I). [8,9] One possible explanation may lie in a slightly lower Ba content in the former samples, which could arise from differences in the solubility of Pb and Ba carbonate

species involved in the precipitation reaction. This could also have an effect on the realisation of an AFE→FE heating transition using chemically prepared samples. For example, an x = 0.075 non-compensated sample shows a AFE→FE but no reverse FE→AFE transition, Table1

Table 1 -Summary of DSC onset and (*peak)* transition temperatures

Composition *x*	PbO content	Transition temperatures (^{o}C)			
	(wt%)	AFE-FE	FE-PE	PE-FE	FE-AFE
0.050	0	152 (*157)*	210 (*213)*	211 (*209)*	73 (*67)*
0.050	3	153 (1*56)*	212 (*215)*	214 (*211)*	76 (*71)*
0.050	5	155 (*161)*	210 (*214)*	212 (*209)*	101 (*94)*
0.075	0	117 (*122)*	204 (*206)*	205 (*202)*	-
0.075	3	110 *(119)*	200 *(205)*	205 *(201)*	32 *(27)*
0.075	5	118 (*124)*	200 (*203)*	202 (*200)*	56 (*53)*
0.100	0	71 (*83)*	193 (*197)*	196 (*193)*	-
0.100	5	73 (*86)*	191 (*195)*	196 (*192)*	4 *(-1)*
0.100	10	73 (*81)*	191 (*195)*	195 (*191)*	-3 *(-8)*
2nd heat /cool		69 (*79)*	191 (*195)*	194 (*191)*	-3 *(-9)*

A 3 wt % starting excess of PbO was sufficient to generate a FE→AFE cooling transition in x = 0.075, with T_{FE-AFE} = 32 °C, Figure 1. The value of T_{FE-AFE} increased to 56 °C for 5 wt % PbO, but with little further change at 10 wt %. In the case of the already reversible x = 0.05 transition, there was an increase in T_{FE-AFE} from 76 °C (for 3 % PbO) to 101 °C at a PbO content of 5 wt % PbO. Transition enthalpy in x = 0.05 increased from 0.84 J/g to 1.49 J/g when the PbO starting excess was raised to 5 wt %. A faint DSC anomaly at ~ 233 °C (peak temperature, heating cycle) occurred in a few samples, irrespective of PbO content. This is attributed to a minor amount of secondary phase $PbZrO_3$ which has been reported previously for $Pb_{1-x}Ba_xZrO_3$ ceramics, and may be due to incomplete reaction.[14]

The effects of excess PbO on ε_r – T plots of an x = 0.075 sample are shown in Figure 2. A dielectric anomaly, consistent with an FE→AFE cooling transition, occurred in 3wt % and 5 wt % excess PbO samples at temperatures comparable to those determined using DSC. The lower peak ε_r value of the 5 wt % PbO example may in part be due to a decrease in density at moderate-high levels of starting excess PbO.[19]

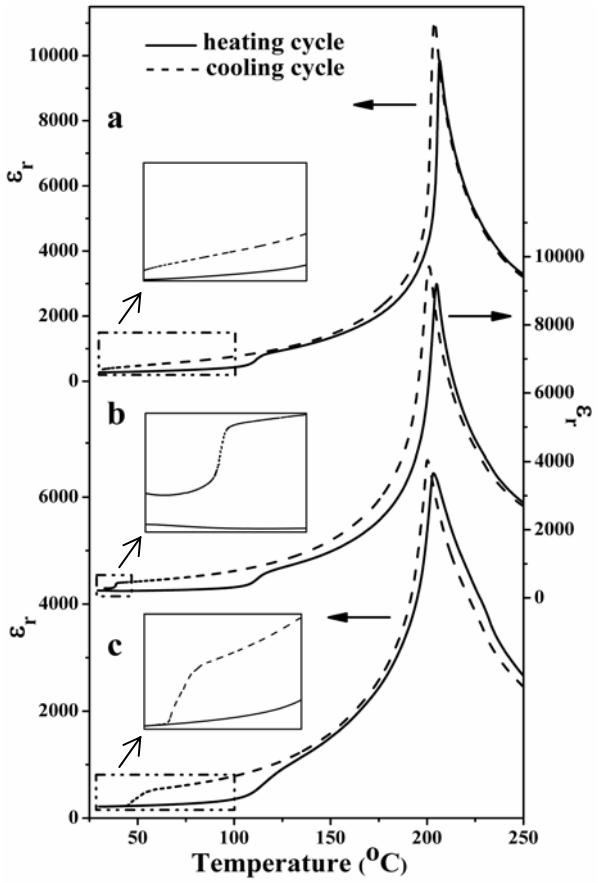


Fig 2. Plot relative permittivity ε_r versus temperature for $Pb_{1-x}Ba_xZrO_3$ x = 0.075: (a) no excess starting PbO, (b) 3 wt % excess PbO, (c) 5 wt% excess PbO.

Chemical analysis by EPMA was conducted on a $Pb_{0.95}Ba_{0.05}ZrO_3$ (nominal) sample. The average Ba and Zr contents were 0.049 and 1.00 (SD ≤ 0.002) confirming the accuracy of the mixed-oxide route in controlling bulk composition.

Without excess starting PbO, the Pb ratio was analysed to be 0.942 (S.D. 0.004), rising to 0.953 (SD 0.005) for samples with 10 wt % excess PbO The EPMA data for Pb, in combination with the foregoing results on changes to phase transition temperatures, are consistent with a slight PbO loss occurring in 'standard' ceramics, and infer that this can be prevented by appropriate excess PbO additions to starting powders. Little or no excess PbO remains after sintering.

5. CONCLUSIONS

In The present results offer a new perspective on $Pb_{1-x}Ba_xZrO_3$ phase transitions, indicating that process-induced Pb^{2+} and O^{2-} lattice vacancies formed at high temperatures due to PbO volatilisation stabilise the rhombohedral FE phase of $Pb_{1-x}Ba_xZrO_3$ ceramics, such that in x = 0.075 or 0.1 no FE→AFE cooling transition occurs. In x = 0.05, the transition is present, but T_{FE-AFE} is lowered by ~25 °C through PbO volatilisation during processing. Additions of excess PbO prior to calcination at 1000 °C overcome phase irreversibility. The mechanism whereby lattice vacancies inhibit the formation of the antiferroelectric crystal structure remains open to question. Transformational strain was thought previously to account for the irreversibility of the AFE→FE transition during heating-cooling cycles.[8,9] It is plausible that some PbO loss may also have occurred in x = 0.1 samples made from chemically precipitated powders, despite the lower calcination temperature, 850 °C. [8,9] Changes in vacancy distribution over time may have contributed to the reported recovery of the AFE phase after long-term ageing. Strain may contribute to the large AFE↔FE temperature hysteresis of the present PbO-compensated samples; however it is not the principal reason for the retention of the FE phase.

REFERENCE

[1] V. J. Tennery, J. Am. Ceram. Soc. **49**, 483 (1966).

[2]B. A. Scott and G. Burns, J. Am. Ceram. Soc. **55**, 331 (1972).

[3]R W Whatmore and A M Glaezer, J Phys.C Solid State Phys. **12,** 1505 (1979).

[4] Z. Xu, X. Dai, D. Viehland, D. Payne, Z. Li, Y Jiang, J.Am.Ceram. Soc. **78,** 2220 (1995).

[5] X Dai, Z. Xu and D Viehland J. Appl. Phys. 77, 5086 (1995).

[6]X. Dai, J. F. Li, and D. Veihland, Phys. Rev. B **51**, 2651 (1995).

[7]H. Futaru, S. Endo, L. C. Ming and H. Fujishita, J. Phys. Chem. Solids **60**, 65 (1999).

[8]B. P. Pokharel and D. Pandey, J. Appl. Phys. **86**, 3327 (1999).

[9]B. P. Pokharel and D. Pandey, J. Appl. Phys. **88**, 5364 (2000).

[10] B. P. Pokharel, R. Ranjan, D. Pandey, V. Siruguri, S. K. Paranjpe, Appl. Phys. Lett. 74 756 (1999).

[11] J H Tseng and T B Wu, Appl. Phys. Lett. 78, 1721 (2001).

[12]Z. Ujma, J. Handerek, M. Pawelczyk and D. Dmytrow, Ferroelectrics **129**, 127 (1992).

[13]K. H. Yoon, S. C. Hwang, and D. H. Kang, J. Mater. Sci. **32**, 17 (1997).

[146] S. Lee, Z-K Liu, M-H Kim and C A Randall, J Appl. Phys. 101, 054119 (2007).

[17] Z Ujma and J Handerek, Phase Trans. **4**, 157 (1984).

18 Z Ujma and J Handerek, Phase Trans. 3, 121 (1983)/

[19]T. Bongkarn, G. Rujijanagul and S. J. Milne, Mater. Lett. **59**, 1200 (2005).

Properties of $(Pb_{0.90}Ba_{0.10})ZrO_3$ Ceramics with Deficient and Excess PbO

Abstract

The effects of excess PbO on the properties of perovskite $(Pb_{0.90}Ba_{0.10})ZrO_3$ (PBZ10) have been investigated. PBZ10 ceramics were prepared by a conventional mixed oxide method. Excess PbO (-1.5, 1, 3, 5 and 10 wt%) was added together with starting materials to compensate for PbO loss from evaporation during calcination and sintering. The XRD results revealed that the fraction of the orthorhombic phase has effected by PbO content. The 3%wt PbO excess sample exhibited the maximum value of relative permittivity at Curie temperature, while the 1%wt PbO excess sample showed maximum value of piezoelectric strain coefficient d_{33} and electromechanical coupling factor k_p.

1. Introduction

Lead zirconate, $PbZrO_3$ (PZ), is an antiferroelectric material which has an orthomrhombic structure at room temperature. The transition to the paraelectric phase(PE) occurs at around 235 °C but a transition from the orthorhombic antiferroelectric (AFE) structure to a rhombohedral ferroelectric (FE) structure occurs a few degrees below the paraelectric transition temperature [1,2]. The temperature range over which the FE phase is stable can be extended by chemical substitution, such as Ba^{2+} on the Pb^{2+} sites to form $(Pb_{1-x}Ba_x)ZrO_3$ (PBZ) solid solutions [3-11]. The substitution of Ba^{2+} for Pb^{2+} in $PbZrO_3$ (PZ) is of considerable interest for transducer applications since its volume change associated with field forced antiferroelectric (AFE) to ferroelectric (FE) transition increases with Ba^{2+} substitution

[10]. Also, the longitudinal strain associated with the AFE to FE transition in these materials can be as large as 0.85%. This makes PBZ ceramic an interesting material for high displacement electromechanical actuator applications [9,10]. Recently, Pokharel *et al.* found an irreversibility of the FE to AFE (FE $\rightarrow$ AFE) phase transition during the cooling cycle in $(Pb_{0.90}Ba_{0.10})ZrO_3$ (PBZ10). An alternative explanation is that the FE$\rightarrow$AFE phase transition is sluggish and the FE phase is quenched to room temperature [9].

It is known that the processing method used to prepare lead-based ceramics is important in influencing phase formation. An important factor which influenced the properties of the lead-based ceramics is the effect of PbO loss due to evaporation during high temperature processing. In case PBZ, it has been suggested that the AFE$\rightarrow$FE transitions are sensitive to the chemical homogeneity of the Ba and Pb ions [10]. Any variation in Pb and O ion vacancy concentrations may be important for phase formation. In the present work, effect of deficient and excess PbO on phase formation of $(Pb_{0.90}Ba_{0.10})ZrO_3$ (PBZ10) was studied. Results were also reported for phase transition and electrical properties.

2. Experimental

The $(Pb_{0.90}Ba_{0.10})ZrO_3$ powders were prepared by a conventional mixed oxide route. The raw materials of PbO, ZrO_2, and $BaCO_3$ were weighed and mixed. Each mixture of the starting powders was milled using zirconia grinding media. After drying and seiving, it was calcined at 850 °C for 6 h. Deficient and excess PbO, equivalent to -1.5, 0, 1, 3, 5, and 10wt%, was applied prior to ball milling before calcination. The powder mixtures were isostatically pressed into pellets then the pellets were sintered at 1325 °C for 4 h in an alumina crucible. In order to help

control PbO loss during sintering (in addition to adding excess PbO) a PZ 'atmosphere' powder was used to generate PbO vapour over the samples. In order to study phase formation, X-ray diffraction analysis (XRD) was performed using a diffractometer with CuK_α radiation. The density of the sintered samples was measured by Archimedes' method with distilled water as the fluid medium. The sintered samples were prepared for electrical properties measurements by first polishing and then gold electrodes were applied to pellets. The dielectric measurements were carried out using an impedance analyzer. For piezoelectric measurement, the samples were poled in silicone oil bath at 170 °C with a field of 25 kV/cm. After poling, the piezoelectric coefficient d_{33} were measured using a d_{33} tester. The electromechanical coupling factor k_p were measured by means of the resonance-anti-resonance method using a precision impedance analyzer then calculated from the resonance and anti-resonance frequencies base on the Onoe's formula [12].

3. Results and discussions

Fig. 1 shows XRD patterns of sintered samples made from different PbO content. The ZrO_2 phase [13] was observed for the 1.5 wt% PbO deficient sample whilst the other samples were shown pure perovskite phase. The formation of ZrO_2 phase may be due to the PbO loss during the sintering process. The absence of PbO in any sample, indicating that the excess PbO beyond that required to maintained compositional control in the PBZ10 powder was eliminated from the sample by volatilization during sintering at 1325 ºC.

The intensity ratio of 004/240 peaks and the relative intensity of superlattice reflections, namely 130/112, 210 and 230/ 212 are plotted in Fig. 2. The intensity ratio of 004/240 peaks may therefore be taken as a qualitative indicator of the relative

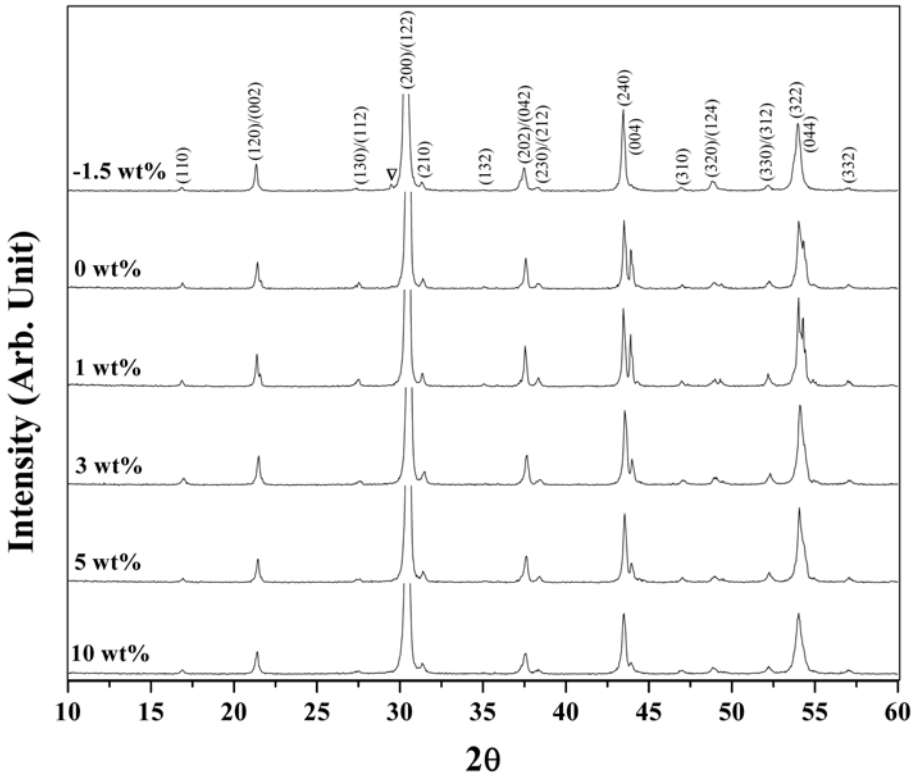
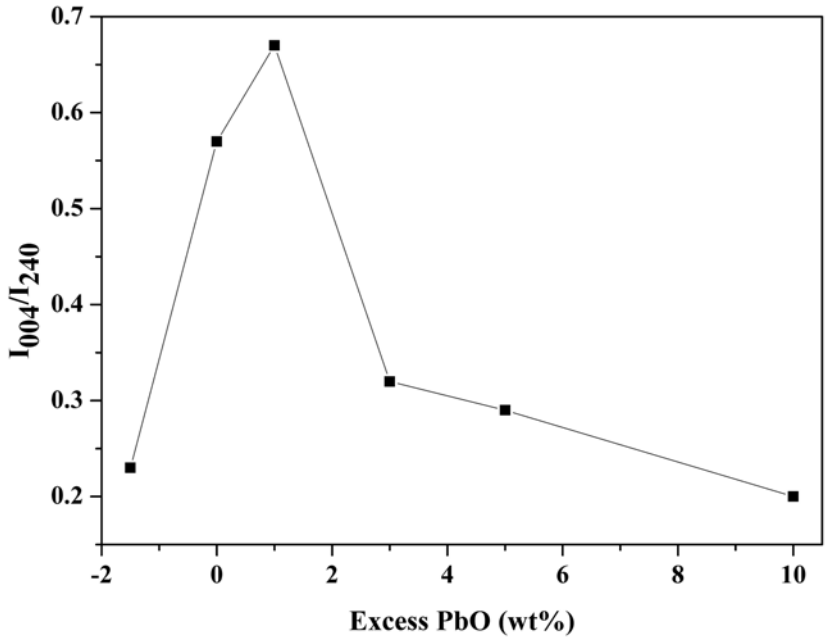
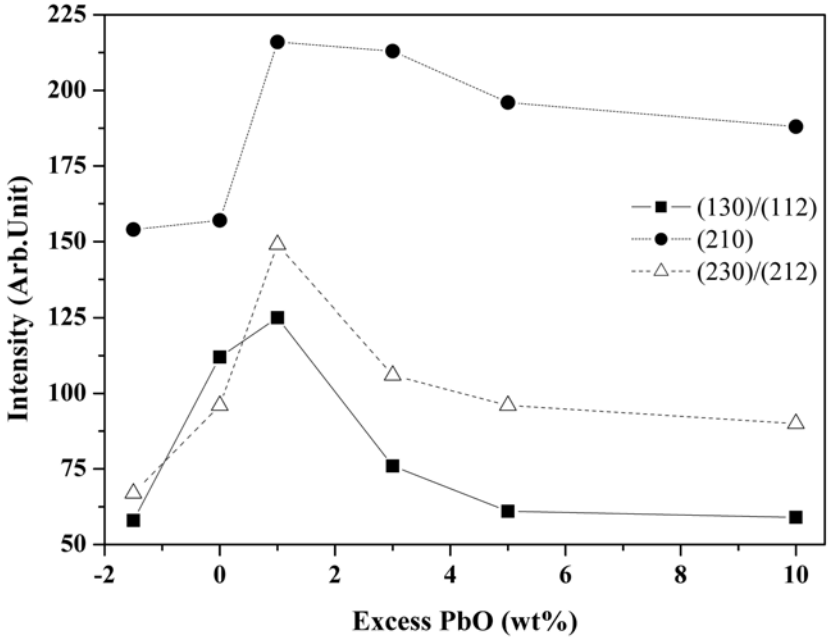


Fig. 1. XRD patterns of PBZ10 ceramics made from starting powder containing different amounts of excess PbO: (∇) ZrO_2 [13].

proportions of orthorhombic (AFE) and rhombohedral (FE) phases. For a purely orthorhombic pattern, the ratio is about 0.5 ($I_{004/240}$ ~0.5). This value decreases with increasing amounts of coexisting rhombohedral phase [9]. The relative intensities of 120/002 and 322/044 peaks also change in a similar manner with increasing proportions of rhombohedral phase. In this work, the intensity ratio of $I_{004/240}$ and the intensities of 130/112, 210 and 230/212 reflections increase with amount of PbO contain up to 1 wt% and then decrease with further increasing amount of PbO content. This indicates that the fraction of the orthorhombic phase has effected by PbO content. The change of the relative proportions of orthorhombic and rhombohedral phases may be due to the change in stoichiometry of the samples [2].



(a)



(b)

Fig.2. (a) Value of intensity ratio, I004/240 for sintered pellets as a function of excess PbO; (b) relative intensity of (130)/(112), (210) and (230)/ (212) XRD peaks as a function of excess PbO.

The temperature dependence of relative permittivity for PBZ10 at various PbO contents is shown in Fig.3. The temperature at which the permittivity is maximum T_c and the relative permittivity at T_c are listed in Table 1. The 1.5 wt% PbO deficient sample presents lower value of the maximum relative permittivity than base composition. There was however an increase in permittivity peak from 11500 for the 0 wt% sample to 12700 for the 3 wt% sample, followed by reductions for the 5 and 10 wt% samples. In addition, the FE $\rightarrow$ PE transition temperature was found between 195 and 197 ºC. The piezoelectric coefficient d_{33} and the electromechanical coupling factor k_p versus amounts of excess PbO at room temperature are shown in Fig. 4. The 1 wt% excess PbO sample exhibits the maximum d_{33} and k_p of 52 pC/N and 0.34, respectively. It can be note that the electrical properties of the ceramics can be related to the density of the samples. The values of sintered density as a function of PbO content are list in Table1. The maximum density was found for the 3 wt. % samples which was ~0.5% higher than for the base composition. However, the density for the 1 wt. % samples was found to close to the 3 wt. % samples. It can be assumed that the 1 and 3 wt% excess PbO produce the optimum density ceramics. For PbO deficient samples, the lower values of the electrical properties can be related to the presence of ZrO_2 as observed in the XRD patterns. However, the reduction of electrical properties in the 5, and 10 wt. % samples match that of the trend of the sintered density. The lowering of density is consistent with there being an excessive amount of PbO in these samples which presents the PbO liquid phase during the sintering. A large amount of PbO liquid phase can produce an initial rapid densification but a lower final density as a result of void formation due to the PbO evaporation as a consequence the porosity of the pellet increases and this porosity is not removed by solid state sintering [14-16].

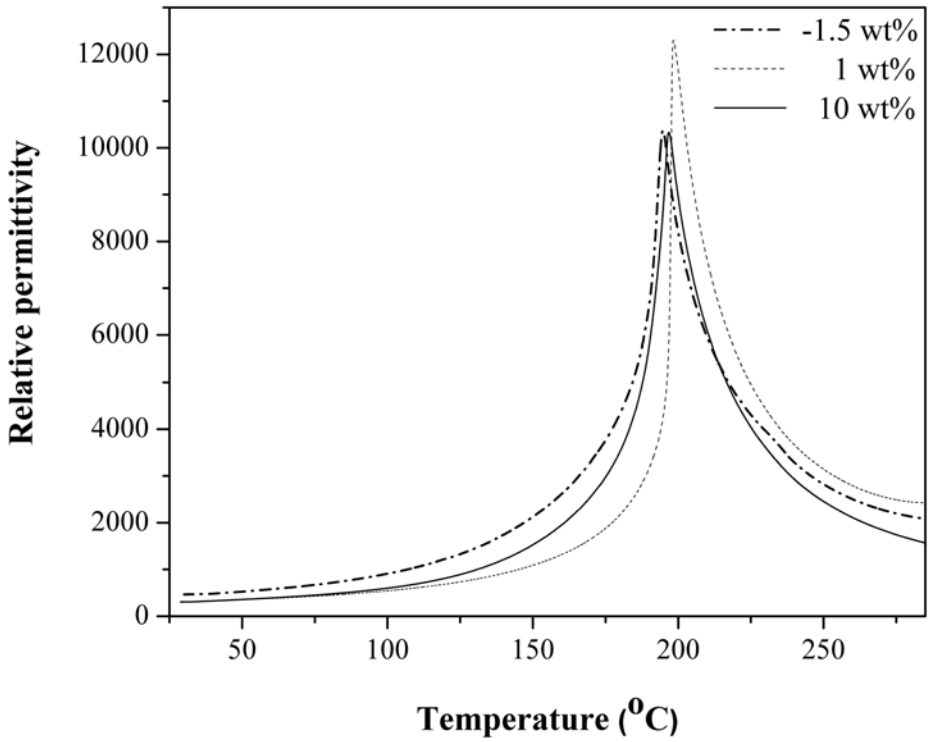


Fig.3. Relative permittivity versus temperature for PBZ10 made from powders with different amount of starting excess PbO.

Table 1 Values of density, Tc, maximum relative permittivity at T_c, and tanδ at T_c of PBZ10 ceramics made from starting powder containing different amounts of excess PbO.

Amount of PbO excess (wt%)	Density(g/cm^3)	T_c(°C)	Maximum relative permittivity at T_c	tanδ at T_c
-1.5	7.64	195	10400	0.0309
0	7.64	197	11500	0.0294
1	7.67	198	12300	0.0785
3	7.68	197	12700	0.0167
5	7.63	196	10600	0.0205
10	7.54	197	10300	0.0015

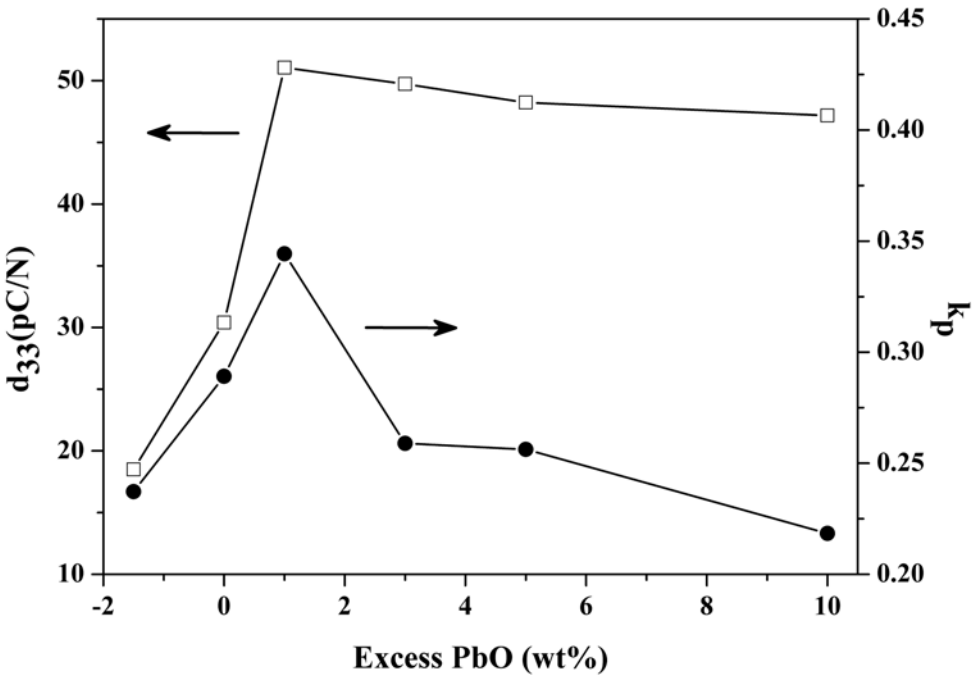


Fig.4. Piezoelectric properties of d_{33} and k_p in PBZ10 ceramics made from powders with different amount of starting excess PbO.

4. Conclusions

In the present work, PBZ10 ceramics were prepared by a conventional mixed oxide method with various excess PbO contents. Effect of deficient and excess PbO on phase formation and electrical properties of PBZ10 ceramic have been studied. The XRD results revealed that the fraction of the rhombohedral phase relative to the orthorhombic phase has effected by PbO content. The 1 and 3 wt% excess PbO were found to produce the maximum density which exhibited the maximum electrical properties of the ceramics.

References

[1] V.J. Tennery, Hihg-temperature phase transitions in $PbZrO_3$, J. Am. Ceram. Soc. 49 (1966) 483-486.

[2] B.A. Scott, G. Burns, Crystal growth and observation of the ferroelectric phase of $PbZrO_3$, J. Am. Ceram. Soc. 55 (1972) 331-333.

[3] G. Shirane, Ferroelectricity and antiferroelectricity in ceramic $PbZrO_3$ containing Ba or Sr, Phys. Rev. 86 (1952) 219-227.

[4] G. Shirane, S. Hoshino, X-ray study of phase transitions in $PbZrO_3$ containing Ba or Sr, Acta Cryst. 7 (1954) 203-210.

[5] I.H. Ismailzade, O.A. Samedov, Influence of permanent electric fields on the successive phase transitions in the solid solutions of the system $(Pb_{1-x}Ba_x)ZrO_3$, Phys. Stat. Sol.(a) 90 (1985) 445-448.

[6] Z. Ujma, J. Handerek, M. Pawelczyk, D. Dmytrow, Phase composition and dielectric properties of lead barium zirconate solid solutions, Ferroelectrics 129 (1992) 127-139.

[7] K.H. Yoon, S.C.Hwang, Dielectric and field-induced strain behaviour of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics, J. Mater. Sci. 32 (1997) 17-21.

[8] B.P. Pokharel, M.K. Datta, D. Pandey, Influence of calcination and sintering temperatures on the structure of $(Pb_{1-x}Ba_x)ZrO_3$, J. Mater. Sci. 34 (1999) 691-700.

[9] B.P. Pokharel, D. Pandey, Irreversibility of the antiferroelectric to ferroelectric phase transition in $(Pb_{0.90}Ba_{0.10})ZrO_3$ ceramics, J. Appl. Phys. 86 (1999) 3327-3332.

[10] B.P. Pokharel, D. Pandey, Dielectric studies of phase transitions in $(Pb_{1-x}Ba_x)ZrO_3$, J. Appl. Phys. 88 (2000) 5364-5372.

[11] B.P. Pokharel, D. Pandey, High temperature x-ray diffraction studies on antiferroelectric and ferroelectric phase transitions in $(Pb_{1-x}Ba_x)ZrO_3$ (x=0.05,0.10), J. Appl. Phys. 90 (2001) 2985-2994.

[12] M. Onoe, H. Juumonji, Useful formulas for piezoelectric ceramic resonators and application to measurement of parameters, J. Acoust. Soc. Am. 47 (1967) 974-980.

[13] Powder Diffraction File no.37-0031, International Centre for Diffraction Data, Newton Square, PA, 2000.

[14] A.I. Kingon, J.B. Clark, Sintering of PZT ceramics: I, atmosphere control, J. Am. Ceram. Soc. 66 (1983) 253-256.

[15] A.I. Kingon, J.B. Clark, Clark, Sintering of PZT ceramics: II, effect of PbO content on densification kinetics, J. Am. Ceram. Soc. 66 (1983) 256-260.

[16] L. Zhou, A. Zimmermann, Y. Zeng, F. Aldinger, Effect of PbO content on the sintering behavior, microstructure, and properties of La-doped PZST antiferroelectric ceramics, J. Mater. Sci.: Mat. Elec. 15 (2004) 145-151.

ภาคผนวก

Available online at www.sciencedirect.com
SCIENCE DIRECT
Current Applied Physics 6 (2006) 319–322
Current Applied Physics
An official journal of the KPS
www.elsevier.com/locate/cap
www.kps.or.kr

Effect of excess PbO on microstructure and mechanical properties of $(Pb_{0.975}Ba_{0.025})ZrO_3$ ceramics

T. Bongkarn [a], G. Rujijanagul [b,*]

[a] Department of Physics, Faculty of Science, Naresuan University, Pitsanulok 65000, Thailand
[b] Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Available online 22 December 2005

Abstract

$(Pb_{0.975}Ba_{0.025})ZrO_3$ (PBZ2.5) ceramics were fabricated from their oxide mixture via the solid state reaction method. Excess PbO (1, 3, 5 and 10 wt%) was added together with starting materials to compensate for PbO loss from evaporation during calcination and sintering. The phase structure was analyzed by XRD. Pure PBZ2.5 phase was observed in all of the PBZ2.5 samples. Density, dielectric and mechanical properties were measured. The experimental results suggest that 1 wt% excess PbO is the optimal level to obtain the best properties of the ceramics. The results were discussed in terms of the mechanisms of densification.

PACS: 62.20.Qp; 77.84.−s

Keywords: Lead barium zirconate; Mechanical properties; Excess lead oxide

1. Introduction

Lead zirconate, $PbZrO_3$ (PZ), is one end member of the industrially interesting solid-solution series $PbZrO_3$–$PbTiO_3$ [1] and the first antiferroelectric identified by Sawaguchi et al. [2,3]. At room temperature PZ is an antiferroelectric phase (AFE) which has an orthorhombic structure [2]. It undergoes the AFE to a paraelectric phase (PE) and transforms from the orthorhombic structure to a cubic structure at 236 °C [4]. It is reported that there exists a ferroelectric phase (FE) over a very narrow temperature range (230–233 °C) [5–8]. The FE intermediate phase can be also introduced by partial replacement of Pb^{2+} ions with Ba^{2+} ions. The temperature range of this intermediate phase also increases with the Ba concentration [9–16]. The AFE–FE phase transition produced the large volume expansion. It makes this material potentially useful for high displacement electromechanical actuator applications [15,16].

It is suggested that PbO loss during firing affects the phase transition of $(Pb_{1-x}Ba_x)ZrO_3$ (PBZ), since the vapor pressure of PbO is quite high above 800 °C [14–16]. Evaporation of PbO also changes the properties of the materials due to the change of stoichiometry. In order to compensate the lead loss in the samples, some excess PbO is usually added during the batch preparation [17–26].

For the past decades, many authors have studied factors that effect on the properties, especially the phase transitions, of PZ and PBZ. Whilst, the microstructure and mechanical properties of PBZ ceramics are of particular importance in the design of displacement electromechanical actuator, they have received much less attention as compared to other active properties. In the present work, effects of PbO on the microstructure and mechanical properties of $(Pb_{0.975}Ba_{0.025})ZrO_3$ (PBZ2.5) were studied. The PBZ2.5 ceramics with different excess of PbO level were synthesized via a solid state route. Microstructure evolution, densification, dielectric properties, and mechanical

* Corresponding author. Fax: +66 53 357312.
E-mail address: rujijanagul@yahoo.com (G. Rujijanagul).

1567-1739/$ - see front matter
doi:10.1016/j.cap.2005.11.009